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(54) **CELLULOSE RESIN AND PROCESS FOR PRODUCING THE SAME**

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See application file for complete search history.

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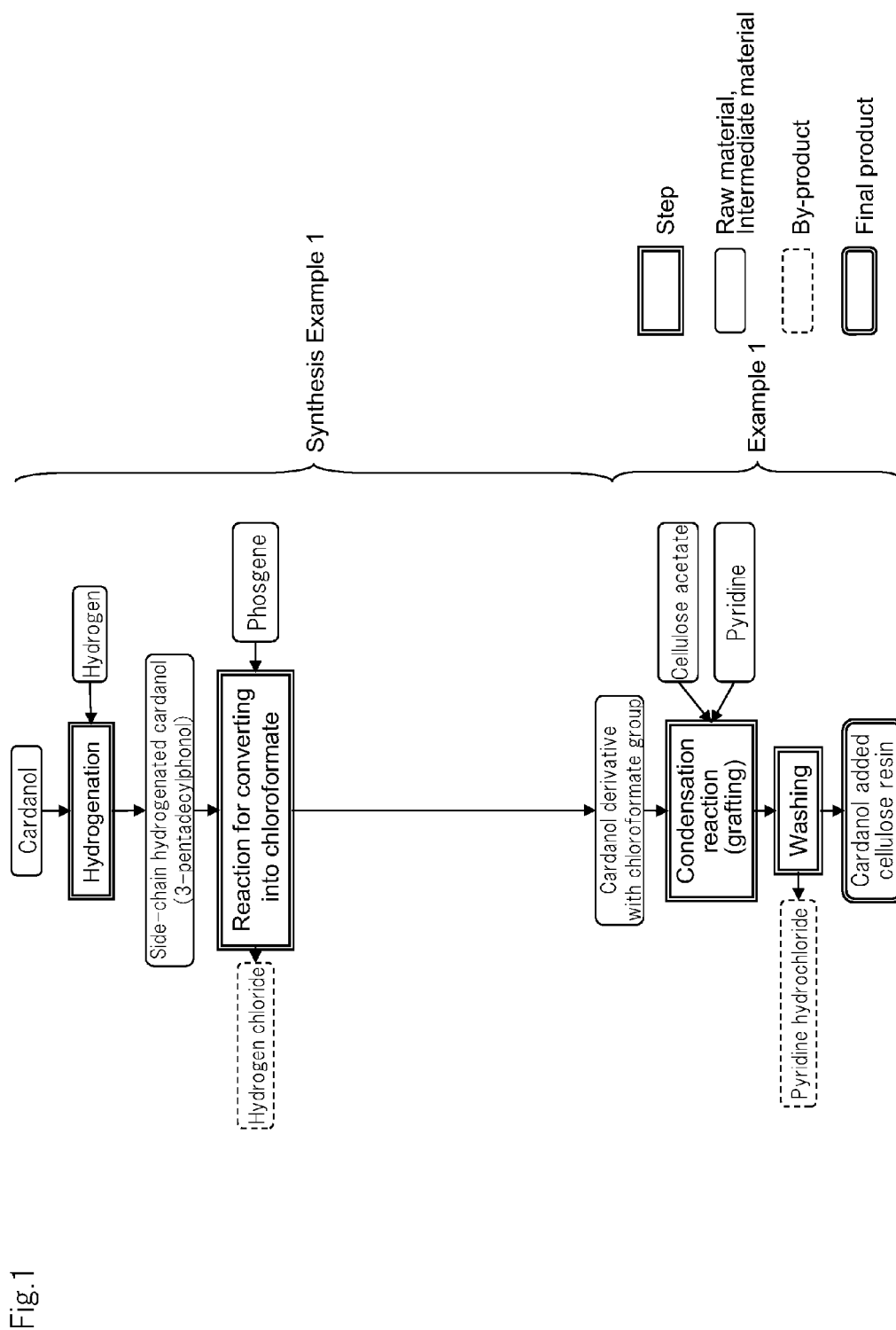
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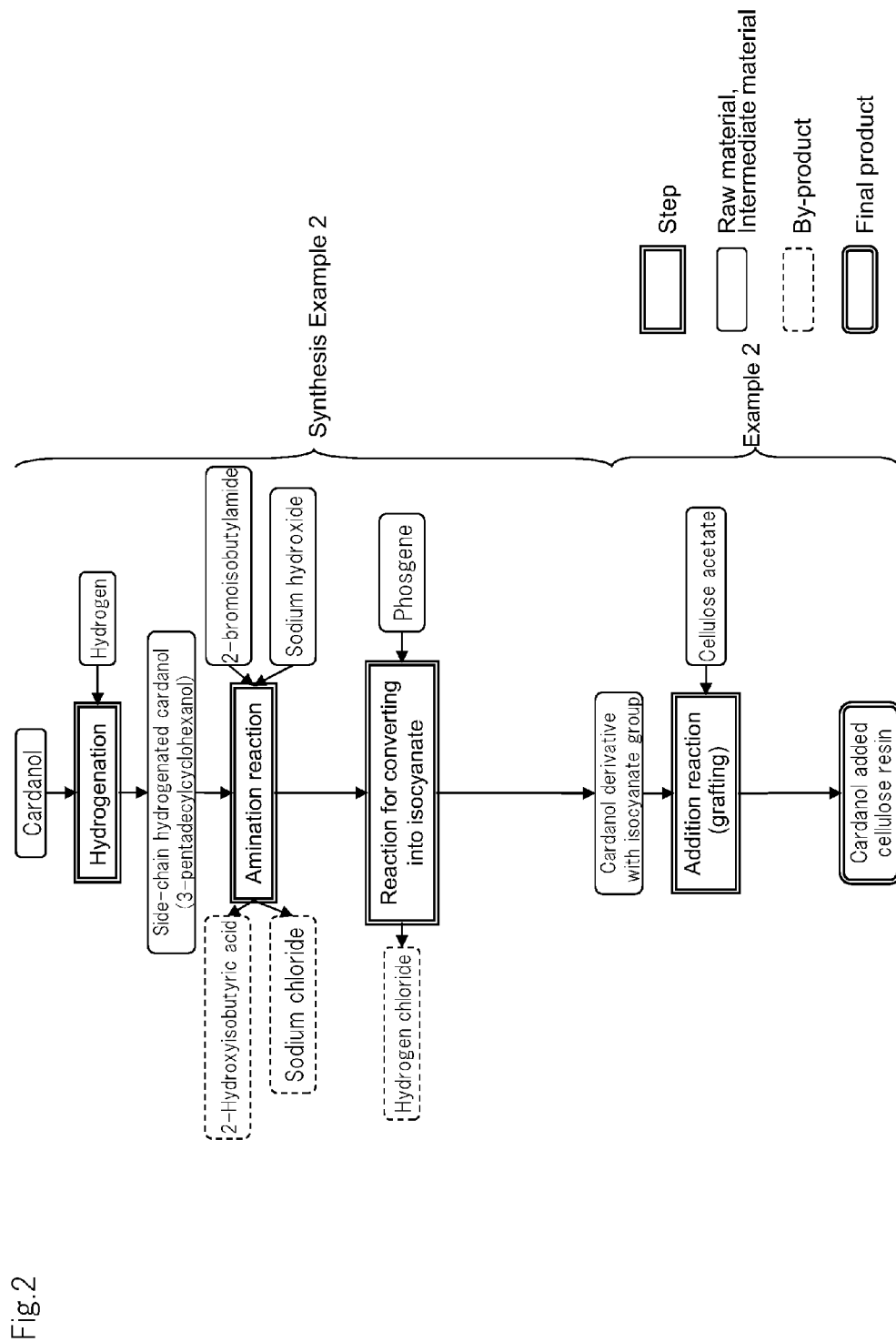
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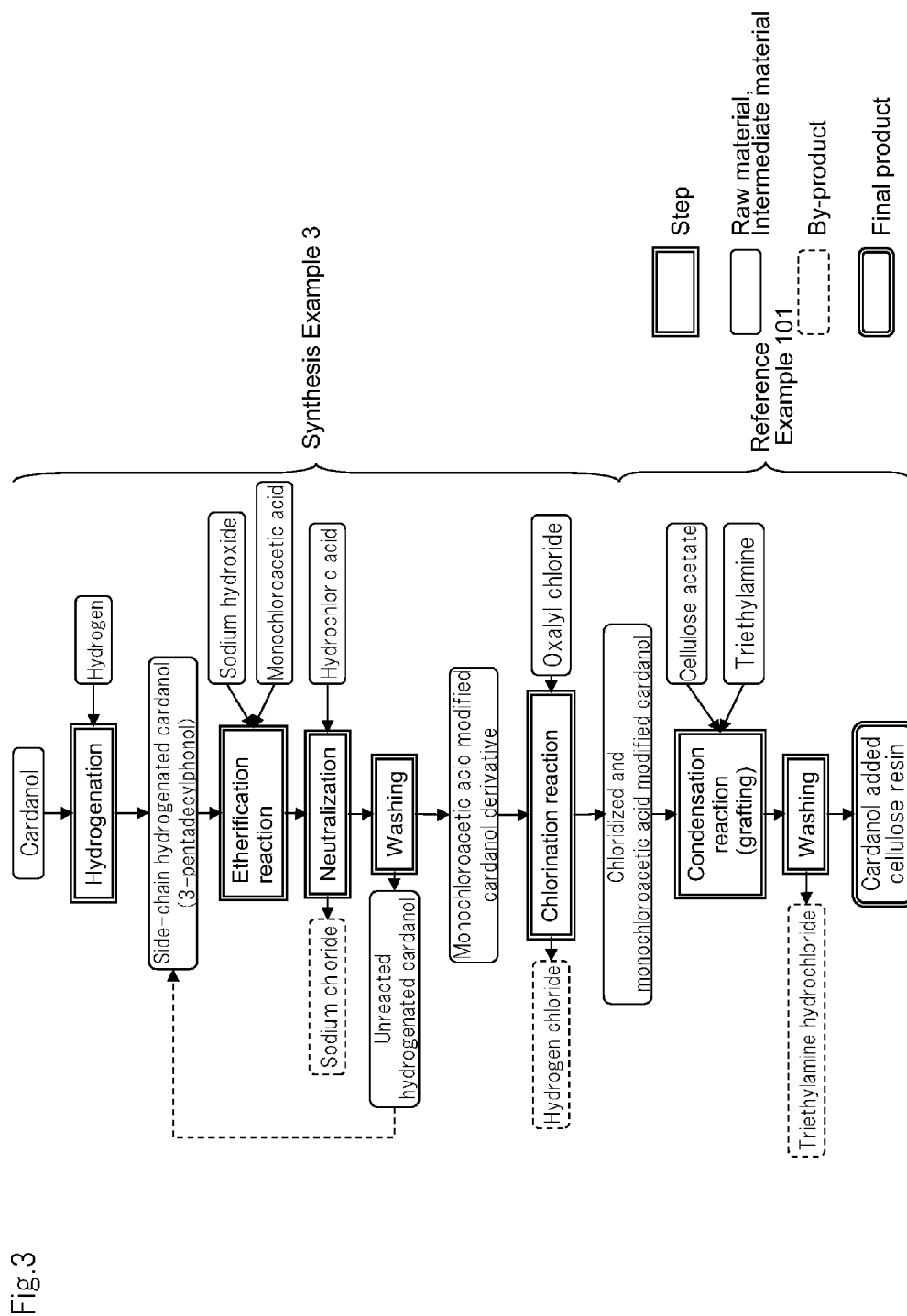
(57) **ABSTRACT**

A cellulose resin produced by binding cellulose or a derivative thereof and cardanol or a derivative thereof by using a hydroxy group of the cellulose or a derivative thereof and a hydroxy group of the cardanol or a derivative thereof, in which carbon atoms to which the hydroxy groups are bound are mutually linked via a carbonate bond or urethane bond formed by using the hydroxy groups.

20 Claims, 3 Drawing Sheets







CELLULOSE RESIN AND PROCESS FOR PRODUCING THE SAME

TECHNICAL FIELD

The present invention relates to a cellulose resin and a process for producing the same.

BACKGROUND ART

Bioplastic using a plant as a raw material can contribute to a countermeasure against petroleum depletion and global warming and has been started being used not only in common products such as packaging, containers and fibers but also in durable products such as electronics and automobiles.

However, general bioplastics, such as polylactic acid, polyhydroxyalkanoate and modified starch, all use starch materials, more precisely, edible parts, as raw materials. Accordingly, for fear of future food shortage, it has been desired to develop a novel bioplastic using a non-edible part as a raw material.

As bioplastic using a non-edible part as a raw material, various types of bioplastics using cellulose, which is a main component of non-edible parts of wood and plant, have been already developed and commercialized.

Cellulose is a high molecular weight compound formed by polymerization of β -glucose. Since cellulose has high crystallinity, it is hard, fragile and absent of thermoplasticity. In addition, since cellulose contains many hydroxy groups, water absorbability is high and water resistance is low. Then, various investigations have been made to improve the properties of cellulose.

For example, Patent Literature 1 (JP11-255801A) discloses a biodegradable graft polymer having thermoplasticity obtained by ring-opening graft polymerization of ϵ -caprolactone with cellulose acetate having a hydroxy group.

Meanwhile, a material using a component of a non-edible part other than cellulose has been developed. For example, cardanol derived from cashew nutshell, since it has stable amount of production and excellent functionality ascribed to its characteristic molecular structure, has found various applications.

As an example of using cardanol, Patent Literature 2 (JP10-8035A) discloses a friction material for brake, which is formed of a fiber base material made of an aramid pulp and a cellulose fiber, and a filler made of calcium carbonate and cashew dust, with the use of a binder made of a phenol resin. Patent Literature 3 (JP2001-32869A) discloses a friction material which is formed of a base material made of an aramid fiber and a cellulose fiber, and a filler made of graphite and cashew dust, with the use of an organic/inorganic composite binder. It is described that the friction material is applied to clutch facing of a power transmission system of automobiles etc.

In Non Patent Literature 1 (George John et al., Polymer Bulletin, 22, p. 89-94 (1989)), it is described that water resistance of paper can be improved by soaking a paper sheet in cardanol to perform a grafting reaction through which cardanol binds to cellulose constituting the paper sheet. It is described that, in the grafting reaction, a terminal double bond of cardanol binds to a hydroxy group of cellulose in the presence of boron trifluoride diethyl ether ($\text{BF}_3\text{---OEt}_2$).

In Non Patent Literature 2 (Emmett M. Partain et al., Polymer Preprints, 39, p. 82-83 (1998)), it is described that water resistance is improved by binding cardanol having an epoxy group introduced therein to hydroxyethylcellulose.

CITATION LIST

Patent Literature

- Patent Literature 1: JP11-255801A
- Patent Literature 2: JP10-8035A
- Patent Literature 3: JP2001-32869A

Non Patent Literature

- Non Patent Literature 1: George John et al., Polymer Bulletin, 22, p. 89-94 (1989)
- Non Patent Literature 2: Emmett M. Partain et al., Polymer Preprints, 39, p. 82-83 (1998)

SUMMARY OF INVENTION

Technical Problem

Cellulose bioplastic, whose properties are influenced by inherent properties of cellulose, is insufficient in strength, heat resistance, water resistance and thermoplasticity. These properties need to be improved particularly when cellulose bioplastic is applied to durable products such as packaging for electronic devices.

Cellulose bioplastic further has the following problems. When a plasticizer is added in order to improve thermoplasticity, heat resistance and strength (in particular, rigidity) decrease and uniformity decreases and bleed out of a plasticizer (a plasticizer bleeds out in the surface of a molded product) occurs. Furthermore, when a plasticizer formed of a petroleum feedstock is added in a large amount, the ratio of plant utilization (vegetism) decreases.

An object of the present invention is to provide a cellulose resin improved in thermoplasticity (moldability), heat resistance, strength and water resistance and having high vegetism and a high ratio of a non-edible part utilization, and to provide a method for easily producing the resin.

Solution to Problem

According to an aspect of the present invention, there is provided a cellulose resin produced by binding cellulose or a derivative thereof and cardanol or a derivative thereof by using a hydroxy group of the cellulose or a derivative thereof and a hydroxy group of the cardanol or a derivative thereof, in which carbon atoms to which the hydroxy groups are bound are mutually linked via a carbonate bond or urethane bond formed by using the hydroxy groups.

According to another aspect of the present invention, there is provided a resin composition containing the aforementioned cellulose resin as a base resin.

According to another aspect of the present invention, there is provided a molding material containing the aforementioned cellulose resin as a base resin.

According to another aspect of the present invention, there is provided a method for producing a cellulose resin, including:

converting a hydroxy group of cardanol or a derivative thereof into a chloroformate group or an isocyanate group to form a modified cardanol, and

reacting the chloroformate group or isocyanate group of the modified cardanol with a hydroxy group of cellulose or a derivative thereof to bind the modified cardanol to the cellulose or a derivative thereof.

Advantageous Effects of Invention

According to an exemplary embodiment, there is provided a cellulose resin improved in thermoplasticity (moldability), heat resistance, strength and water resistance and having high vegetism and a high ratio of a non-edible part utilization, and provided a method for easily producing the resin.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a process chart of a cellulose resin according to an Example of the present invention.

FIG. 2 is a process chart of a cellulose resin according to another Example of the present invention.

FIG. 3 is a process chart of a cellulose resin according to Reference Examples.

DESCRIPTION OF EMBODIMENTS

The cellulose resin according to an exemplary embodiment of the present invention is prepared by directly binding cellulose (or a derivative thereof) and cardanol (or a derivative thereof) via a carbonate bond or a urethane bond, which is formed by using a hydroxy group of the cellulose (or a derivative thereof) and a hydroxy group of the cardanol (or a derivative thereof). Hereinafter, binding (addition) of cardanol (or a derivative thereof) to cellulose (or a derivative thereof) is appropriately referred to as "grafting".

Owing to such grafting, mechanical characteristics (particularly toughness) and water resistance can be improved. Furthermore, since good thermoplasticity is provided by the grafting, the amount of plasticizer to be added can be reduced or a plasticizer may not be added. As a result, heat resistance and strength (particularly rigidity) can be suppressed from reducing compared to the cellulose resin containing a plasticizer, and homogeneity of the resultant resin can be improved. In addition, a problem of bleed out can be overcome. Furthermore, since the addition amount of plasticizer made of a petroleum feedstock can be lowered or reduced to zero, the ratio of plant utilization can be increased. In addition, since cellulose and cardanol are both derived from a non-edible part of a plant, utilization of a non-edible part can be enhanced.

Furthermore, by binding cellulose (or a derivative thereof) and cardanol (or a derivative thereof) directly with a carbonate bond or a urethane bond, strength can be further improved compared to the case where binding is made via an organic linking group.

Furthermore, a grafted cellulose resin can be easily produced by converting the hydroxy group of cardanol or a derivative thereof into a chloroformate group or an isocyanate group and binding the obtained modified cardanol (cardanol

with a chloroformate group or cardanol with an isocyanate group) to cellulose or a derivative thereof.

As a cardanol or a derivative thereof, it is preferable to use a hydrogenated cardanol obtained by hydrogenating cardanol.

In the cellulose resin according to an exemplary embodiment of the present invention, the number of cardanol molecules (or a derivative thereof) to be added per glucose unit, DS_{CD} , is preferably 0.1 or more.

Furthermore, the number of remaining hydroxy groups per glucose unit, DS_{OH} , is preferably 0.9 or less.

To a hydroxy group of cellulose or a derivative thereof, a reactive hydrocarbon compound having a functional group capable of reacting with the hydroxy group can be added. As the reactive hydrocarbon compound, compounds having a carboxyl group, a carboxylic halide group, a carboxylic acid anhydride group and an isocyanate group can be used. As the reactive hydrocarbon compound, an aliphatic monocarboxylic acid, an aromatic monocarboxylic acid, alicyclic monocarboxylic acid, each of the acid halides or acid anhydrides of these monocarboxylic acids, an aliphatic monoisocyanate, an aromatic monoisocyanate and an alicyclic monoisocyanate can be used. The number of the reactive hydrocarbon compounds to be added per glucose unit, DS_{XC} , can be set at 0.1 or more.

Furthermore, at least one type of acyl group selected from an acetyl group, a propionyl group and a butyryl group can be added to the hydroxy group of cellulose or a derivative thereof. The number of the acyl groups to be added per glucose unit, DS_{AC} , can be set at 0.5 or more.

Furthermore, at least one type of first acyl group selected from an acetyl group, a propionyl group and a butyryl group and at least one type of second acyl group derived from a monocarboxylic acid selected from an aromatic carboxylic acid and an alicyclic carboxylic acid can be added to a hydroxy group of cellulose or a derivative thereof. The number of the first acyl group to be added per glucose unit, DS_{AC} , can be set at 0.5 or more and the number of the second acyl group to be added per glucose unit, DS_{XC} , can be set at 0.1 or more.

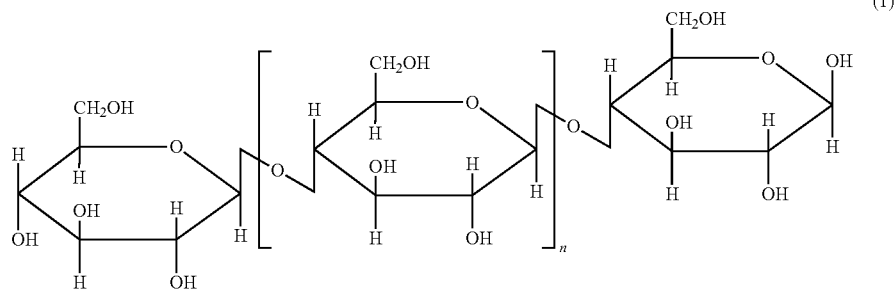
Furthermore, the total amount of cellulose component and cardanol component is preferably 50% by mass or more based on the whole resin.

The resin composition according to an exemplary embodiment of the present invention contains a cellulose resin as a base resin and can further contain a thermoplastic polyurethane elastomer or a modified silicone compound.

[Cellulose or a Derivative Thereof]

Cellulose is a straight-chain polymer of β -glucose, represented by the following formula (1) and each glucose unit has three hydroxy groups. Using these hydroxy groups, cardanol (or a derivative thereof) can be grafted.

[Formula 1]



Cellulose is a main component of a plant and can be obtained by a separation treatment for removing other components such as lignin from a plant. Other than the cellulose thus obtained, cellulose obtained by purification of cotton or pulp rich in cellulose content can be used, or the cotton or pulp can be directly used.

The polymerization degree of cellulose (or a derivative thereof) preferably falls within the range of 50 to 5000 and more preferably 100 to 3000 in terms of glucose polymerization degree. If the polymerization degree is extremely low, the strength and heat resistance of the produced resin may not be sufficient in some cases. Conversely, if the polymerization degree is extremely high, the melt viscosity of the produced resin is extremely high, interfering with molding in some cases.

Cellulose (or a derivative thereof) may be mixed with chitin and chitosan having an analogous structure. When cellulose is mixed with them, the amount thereof is preferably 30% by mass or less relative to the total amount of mixture, preferably 20% by mass or less and further preferably 10% by mass or less.

A cellulose derivative herein refers to cellulose having hydroxy groups partly acylated, etherified or grafted. Specific examples thereof include organic acid esters such as cellulose acetate, cellulose butyrate and cellulose propionate; inorganic acid esters such as cellulose nitrate, cellulose sulfate and cellulose phosphate; mixed esters such as cellulose acetate propionate, cellulose acetate butyrate, cellulose acetate phthalate and cellulose acetate nitrate; and etherified cellulose such as methylcellulose, hydroxyethylcellulose and hydroxypropylcellulose. Furthermore, celluloses grafted with styrene, (meth)acrylic acid, (meth)acrylate, ϵ -caprolactone, lactide, glycolide, etc. These acylated cellulose, etherified cellulose and grafted cellulose may be used singly or in combination of two or more types.

As the cellulose (or a derivative thereof) of the exemplary embodiment, for example, at least one acylated cellulose selected from a cellulose acetate, cellulose propionate and cellulose butyrate which have a part of the hydroxy groups acylated can be preferably used.

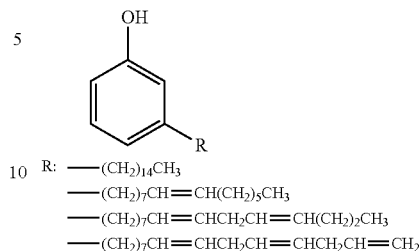
The term "cellulose derivative" used herein includes both a cellulose compound and a compound having a cellulose skeleton obtained by biologically or chemically introducing a functional group into raw-material cellulose.

[Grafting of Cardanol or a Derivative Thereof]

Cardanol, which is a component contained in the cashew nut shell, is an organic compound composed of a phenol moiety and a straight-chain hydrocarbon moiety as shown in the following formula (2). There are 4 types of cardanols different in the number of unsaturated bonds in the straight-chain hydrocarbon moiety R. Usually, cardanol is a mixture of these 4 components. To be more specific, cardanol is a mixture of 3-pentadecylphenol, 3-pentadecylphenol monoene, 3-pentadecylphenol diene and 3-pentadecylphenol triene, described in the following formula (2). Cardanol obtained by extracting and purifying from a cashew nutshell liquid can be used.

[Formula 2]

(2)



15 The straight-chain hydrocarbon moiety of cardanol contributes to improving flexibility and hydrophobicity of a resin, whereas the phenol moiety has a highly reactive hydroxy group for use in grafting. When such cardanol (or a derivative thereof) is grafted to cellulose (or a derivative thereof), cardanol (or a derivative thereof) is added like bristles to form a brush-form cellulose structure. As a result, cardanol bristles thus grafted interact with each other to improve mechanical characteristics (particularly toughness), as well as to impart thermoplasticity. In addition, owing to hydrophobicity of cardanol, water resistance can be improved.

Grafting is performed by converting the hydroxy group of cardanol (or a derivative thereof) to a functional group capable of easily reacting with a hydroxy group of cellulose (or a derivative thereof), i.e., a chloroformate group (—OCOCI) or an isocyanate group (—NCO), and reacting the functional group with the hydroxy group of cellulose (or a derivative thereof). As a result, the cellulose carbon atom to which the hydroxy group of cellulose (or a derivative thereof) is bound, and the cardanol carbon atom to which the hydroxy group of cardanol (or a derivative thereof) is bound, are linked via a carbonate bond (—OCOO—) or a urethane bond (—NHCOO—). More specifically, one of the carbonate bond or the urethane bond directly connects to the cellulose carbon atom; whereas the other bond directly connects to the cardanol carbon atom. According to such grafting, the efficiency of a grafting reaction can be improved and a side reaction can be suppressed. Furthermore, strength can be further improved from the grafted cellulose resin obtained by linking cellulose and cardanol via an organic linking group.

Grafting is, for example, performed as follows. First, the hydroxy group of cardanol (or a derivative thereof) is converted to a chloroformate group or an isocyanate group to obtain a modified cardanol (cardanol with a chloroformate group or cardanol with an isocyanate group). Subsequently, the obtained modified cardanol and cellulose (or a derivative thereof) are reacted, more specifically, a hydroxy group of the cellulose (or a derivative thereof) and the functional group (chloroformate group or isocyanate group) of the modified cardanol are reacted, to form a carbonate bond or a urethane bond. In this manner, grafting can be made.

According to the aforementioned grafting, the hydroxy group of cellulose (or a derivative thereof) and the hydroxy group of cardanol (or a derivative thereof) are eliminated to form a graft bond; at the same time, the hydrophobic structure of cardanol can be introduced into cellulose (or a derivative thereof) to improve water resistance.

To graft cardanol (or a derivative thereof) to cellulose (or a derivative thereof), the hydroxy group of cardanol and a hydroxy group of cellulose are preferably used as mentioned above in view of efficiency of a grafting reaction, resultant molecular structure and water resistance. Since such grafting

is made by use of a highly-reactive hydroxy group, more efficient grafting can be realized compared to grafting using an unsaturated bond (double bond) of the straight-chain hydrocarbon moiety of cardanol. Furthermore, according to the grafting of the exemplary embodiment, since the phenol moiety of cardanol reacts with cellulose and fixed to it, interaction between mutual straight-chain hydrocarbon moieties of the grafted cardanol molecules enhances, and thus a desired effect of improving mechanical characteristics can be obtained. Furthermore, in the exemplary embodiment, since grafting is performed by eliminating the hydroxy group of cardanol, water resistance can be improved (suppressing water absorbability). From this point of view, the grafting of the exemplary embodiment is advantageous compared to grafting that does not use a hydroxy group.

The above cardanol with a chloroformate group is obtained by converting the hydroxy group of cardanol (or a derivative thereof) into a chloroformate group. A method of converting the hydroxy group to a chloroformate group is not particularly limited and a method generally known in the art can be used. For example, by introducing phosgene in an inactive organic solvent, the hydroxy group of cardanol (or a derivative thereof) can be converted into a chloroformate group in a single step.

The cardanol with an isocyanate group is obtained by converting the hydroxy group of cardanol (or a derivative thereof) into an isocyanate group. A method for converting the hydroxy group into an isocyanate group is not particularly limited and a method generally known in the art can be used. Examples of the method include a method of converting the hydroxy group into an isocyanate group by reacting ammonia at high temperature and high pressure in the presence of a sodium hydrogen sulfite as a catalyst to convert the hydroxy group of cardanol (or a derivative thereof) into an amino group (Bucherer reaction) and introducing phosgene into this to obtain the isocyanate group, and a method of converting the hydroxy group into an isocyanate group by converting the hydroxy group of cardanol (or a derivative thereof) into an amino group by a reaction through alkylation with 2-bromoisobutylamine, transposition (Smiles rearrangement) under alkaline conditions and hydrolysis, and then introducing phosgene to obtain the isocyanate group.

As a result of grafting using cardanol with a chloroformate group, the cellulose carbon atom to which a hydroxy group of cellulose (or a derivative thereof) is bound, and the cardanol carbon atom to which the hydroxy group of cardanol (or a derivative thereof) is bound, are linked via a carbonate bond. As a result of grafting using cardanol with an isocyanate group, the cellulose carbon atom to which a hydroxy group of cellulose (or a derivative thereof) is bound, and the cardanol carbon atom to which the hydroxy group of cardanol (or a derivative thereof) is bound, are linked via an urethane bond.

In cardanol, it is preferable that the unsaturated bond (double bond) of the straight-chain hydrocarbon moiety of cardanol is hydrogenated and converted into a saturated bond. The conversion rate (hydrogenation rate) of the unsaturated bond by hydrogenation is preferably 90% by mole or more and more preferably 95% by mole or more. The ratio of the remaining unsaturated bond in cardanol (the number of unsaturated bonds per cardanol molecule) after hydrogenation is preferably 0.2 bonds/molecule or less and more preferably 0.1 bond/molecule or less. Furthermore, the aromatic ring of the phenol moiety of cardanol may be hydrogenated and converted into a cyclohexane ring.

When cardanol (or a derivative thereof) in which a large number of unsaturated bonds still remain in the straight-chain hydrocarbon moiety, is grafted to cellulose (or a derivative

thereof), a side reaction is likely to occur, with the result that grafting cannot be efficiently performed and the solubility of a grafted product in a solvent may often significantly reduce. When a cardanol derivative, in which an unsaturated bond(s) of the straight-chain hydrocarbon moiety are sufficiently converted into saturated bonds by hydrogenation, is grafted, grafting can be efficiently performed whereas a side reaction is suppressed and in addition, reduction of solubility of a grafted product in a solvent can be suppressed. Furthermore, if a cardanol derivative in which the aromatic ring of the phenol moiety of cardanol is fully converted into a cyclohexane ring, the lightness of color of the grafted product can be improved.

The hydrogenation method is not particularly limited and a method known in the art can be used. As the catalyst, a precious metal such as palladium, ruthenium, rhodium and platinum or nickel, or a metal selected from these immobilized on a carrier such as activated carbon, activated alumina and diatom earth is mentioned. As the reaction system, a batch system, in which a reaction is performed while suspending and stirring a powdery catalyst, and a continuous system using a reaction tower charged with a molded catalyst, can be employed. The solvent for hydrogenation may not be used depending upon the system of hydrogenation. However, when a solvent is used, alcohols, ethers, esters and saturated hydrocarbons are generally mentioned. The reaction temperature for hydrogenation is not particularly limited; however, it can be usually set at 20 to 250° C. and preferably 50 to 200° C. If the reaction temperature is excessively low, a hydrogenation rate becomes low. Conversely, if the reaction temperature is excessively high, the amount of decomposition product may increase. The hydrogen pressure during the hydrogenation can be usually set at 10 to 80 kgf/cm² (9.8×10⁵ to 78.4×10⁵ Pa) and preferably 20 to 50 kgf/cm² (19.6×10⁵ to 49.0×10⁵ Pa).

Hydrogenation can be performed before a modified cardanol is formed, after a modified cardanol is formed and before the modified cardanol is grafted, or after a modified cardanol is grafted. In view of the reaction efficiency of hydrogenation and grafting reaction, hydrogenation is preferably performed before a modified cardanol is grafted and further preferably before a modified cardanol is formed.

The ratio (grafting rate) of cardanol (or a derivative thereof) bound to cellulose (or a derivative thereof) relative to the cellulose (or a derivative thereof) is represented by the number (DS_{CD}) (average value) of cardanol molecules (or a derivative thereof) to be added per glucose unit of cellulose (or a derivative thereof), in other words, the number of hydroxy groups bound to cardanol molecules (or a derivative thereof) (the degree of substitution of the hydroxy group) (average value). DS_{CD} is preferably 0.1 or more and more preferably 0.2 or more. DS_{CD} may be set to 0.4 or more. When DS_{CD} is excessively low, the effect by grafting may not be sufficiently obtained.

The maximum value of DS_{CD} is theoretically "3"; however, in view of facilitating production (grafting), DS_{CD} is preferably 2.5 or less, more preferably 2 or less and further preferably 1.5 or less. Furthermore, DS_{CD} may be 1 or less. Even in this case, sufficient improvement effect can be obtained. If DS_{CD} increases, tensile breaking strain (toughness) increases; whereas, the maximum strength (tensile strength, bending strength) tends to decrease. Therefore, DS_{CD} is preferably set appropriately in accordance with desired properties.

[Grafting of Reactive Hydrocarbon Compounds]

Cardanol (or a derivative thereof) is grafted and simultaneously, a specific reactive hydrocarbon compound may be

grafted to cellulose (or a derivative thereof). Owing to this, a cellulose resin can be improved so as to have desired properties.

This reactive hydrocarbon compound is a compound having at least one functional group capable of reacting with a hydroxy group of cellulose (or a derivative thereof). Examples thereof include hydrocarbon compounds having a carboxyl group, a carboxylic halide group, a carboxylic acid anhydride group, an isocyanate group, a chloroformate group or an acryl group. Specific examples thereof include at least one compound selected from monocarboxylic acids such as an aliphatic monocarboxylic acid, an aromatic monocarboxylic acid and an alicyclic monocarboxylic acid, and acid halides or acid anhydrides thereof; at least one compound selected from an aliphatic monoisocyanate, an aromatic monoisocyanate and an alicyclic monoisocyanate; at least one compound selected from an aliphatic monochloroformate, an aromatic monochloroformate and an alicyclic monochloroformate; an acrylic acid ester; and a methacrylic acid ester.

As the aliphatic monocarboxylic acid, a straight or branched (having a side chain) fatty acid is mentioned. Examples of the aromatic monocarboxylic acid include an aromatic monocarboxylic acid having a carboxyl group directly bound to an aromatic ring and an aromatic monocarboxylic acid having a carboxyl group bound to the aromatic ring via an alkylene group (for example, methylene group, ethylene group) (the acid having an aliphatic carboxylic acid group bound to the aromatic ring). Examples of the alicyclic monocarboxylic acid include an alicyclic monocarboxylic acid having a carboxyl group directly bound to an alicycle and an alicyclic monocarboxylic acid having a carboxyl group bound to an alicycle (an aliphatic carboxylic acid group bound to the alicycle) via an alkylene group (for example, methylene group, ethylene group) (the acid having an aliphatic carboxylic acid group bound to an alicycle).

Examples of the aliphatic monoisocyanate include an aliphatic monoisocyanate having an isocyanate group bound to a straight aliphatic hydrocarbon or a branched aliphatic hydrocarbon having a side chain. Examples of the aromatic monoisocyanate include an aromatic monoisocyanate having an isocyanate group directly bound to an aromatic ring and an aromatic monoisocyanate having an isocyanate group bound to an aromatic ring via an alkylene group (for example, a methylene group or an ethylene group) (the aromatic monoisocyanate having an aliphatic isocyanate group bound to an aromatic ring). Examples of the alicyclic monoisocyanate include an alicyclic monoisocyanate having an isocyanate group directly bound to an alicycle and an alicyclic monoisocyanate having an isocyanate group bound to an alicycle via an alkylene group (for example, a methylene group or an ethylene group) (the alicyclic monoisocyanate having an aliphatic isocyanate group bound to an alicycle).

Examples of the aliphatic monochloroformate include an aliphatic monochloroformate having a chloroformate group bound to a straight aliphatic hydrocarbon or a branched aliphatic hydrocarbon having a side chain. Examples of the aromatic monochloroformate include an aromatic monochloroformate having a chloroformate group directly bound to an aromatic ring and an aromatic monochloroformate having a chloroformate group bound to an aromatic ring via an alkylene group (for example, a methylene group or an ethylene group) (the aromatic monochloroformate having an aliphatic chloroformate group bound to an aromatic ring). Examples of the alicyclic monochloroformate include an alicyclic monochloroformate having a chloroformate group directly bound to an alicycle and an alicyclic monochloroformate

having a chloroformate group bound to an alicycle via an alkylene group (for example, a methylene group or an ethylene group) (the alicyclic monochloroformate having an aliphatic chloroformate group bound to an alicycle).

The reactive hydrocarbon compound preferably has carbon atoms within the range of 1 to 32 and more preferably within the range of 1 to 20. If the number of carbon atoms is excessively large, the size of the molecule becomes excessively large and reaction efficiency decreases due to steric hindrance. As a result, it becomes difficult to increase a grafting rate.

The reactive hydrocarbon compound is effective in improving properties in the case where it is particularly arranged so as to bury gaps in a sterical structure of a grafted cardanol (or a derivative thereof).

When the hydrocarbon group of the reactive hydrocarbon compound is an aromatic hydrocarbon group and an alicyclic hydrocarbon group, it efficiently works to particularly improve rigidity and heat resistance. When the hydrocarbon group is an aliphatic hydrocarbon group, it efficiently works to particularly improve toughness.

Examples of the aliphatic monocarboxylic acid to be used as the reactive hydrocarbon compound include saturated fatty acids such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, 2-ethyl-hexanecarboxylic acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, heptadecylic acid, stearic acid, nonadecanoic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, heptacosanoic acid, montanic acid, melissic acid and lacceric acid; unsaturated fatty acids such as butenoic acid, pentenoic acid, hexenoic acid, octenoic acid, undecylenic acid, oleic acid, sorbic acid, linoleic acid, linolenic acid and arachidonic acid; and derivatives of these. These may further have a substituent.

Examples of the aromatic monocarboxylic acid used as the reactive hydrocarbon compound include an aromatic carboxylic acid having a carboxyl group introduced in a benzene ring such as benzoic acid; an aromatic carboxylic acid having an alkyl group introduced in a benzene ring such as toluic acid; an aromatic carboxylic acid having an aliphatic carboxylic acid group introduced in a benzene ring such as phenylacetic acid and phenyl propionic acid; an aromatic carboxylic acid having two or more benzene rings such as biphenylcarboxylic acid and biphenylacetic acid; an aromatic carboxylic acid having a condensed-ring structure such as naphthalene carboxylic acid and tetralin carboxylic acid; and derivatives of these.

Examples of the alicyclic monocarboxylic acid to be used as the reactive hydrocarbon compound include an alicyclic monocarboxylic acid having a carboxyl group introduced to an alicycle such as cyclopentane carboxylic acid, cyclohexane carboxylic acid and cyclooctane carboxylic acid; alicyclic monocarboxylic acids having an aliphatic carboxylic acid introduced in an alicycle such as cyclohexyl acetic acid; and derivatives of these.

Examples of the aliphatic monoisocyanate used as the reactive hydrocarbon compound include saturated aliphatic isocyanates such as methyl isocyanate, ethyl isocyanate, propyl isocyanate, isopropyl isocyanate, butyl isocyanate, pentyl isocyanate, hexyl isocyanate, heptyl isocyanate, octyl isocyanate, nonyl isocyanate, decyl isocyanate and dodecyl isocyanate; unsaturated aliphatic isocyanates such as butenyl isocyanate, pentenyl isocyanate, hexenyl isocyanate, octenyl isocyanate and dodecenyl isocyanate; and derivatives of these. These may further have a substituent.

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Examples of the aromatic monoisocyanate used as the reactive hydrocarbon compound include an aromatic monoisocyanate having an isocyanate group introduced in a benzene ring, such as phenyl isocyanate; an aromatic monoisocyanate having an alkyl group introduced in a benzene ring, such as tolyl isocyanate; an aromatic monoisocyanate having an aliphatic isocyanate group introduced in a benzene ring, such as phenylmethyl isocyanate and phenylethyl isocyanate; an aromatic isocyanate having two or more benzene rings, such as biphenyl isocyanate and biphenylmethyl isocyanate; aromatic isocyanate having a condensation ring structure, such as naphthalene isocyanate and tetralin isocyanate; and derivatives of these.

Examples of the alicyclic monoisocyanate used as the reactive hydrocarbon compound include an alicyclic monoisocyanate having an isocyanate group introduced in an alicycle, such as cyclopentyl isocyanate, cyclohexyl isocyanate and cyclooctyl isocyanate; an alicyclic monoisocyanate having an aliphatic isocyanate group introduced in an alicycle, such as cyclohexylmethyl isocyanate; and derivatives of these.

Examples of the aliphatic monochloroformate used as the reactive hydrocarbon compound include saturated aliphatic chloroformates such as methyl chloroformate, ethyl chloroformate, propyl chloroformate, isopropyl chloroformate, butyl chloroformate, pentyl chloroformate, hexyl chloroformate, heptyl chloroformate, octyl chloroformate, nonyl chloroformate, decyl chloroformate and dodecyl chloroformate; unsaturated aliphatic chloroformates such as butenyl chloroformate, pentenyl chloroformate, hexenyl chloroformate, octenyl chloroformate and dodecenyl chloroformate; and derivatives of these. These may further have a substituent.

Examples of the aromatic monochloroformate used as the reactive hydrocarbon compound include an aromatic monochloroformate having a chloroformate group introduced in a benzene ring, such as phenyl chloroformate; an aromatic monochloroformate having an alkyl group introduced in a benzene ring, such as tolyl chloroformate; an aromatic monochloroformate having an aliphatic chloroformate group introduced in a benzene ring, such as phenylmethyl chloroformate and phenylethyl chloroformate; an aromatic chloroformate having two or more benzene rings, such as biphenyl chloroformate and biphenylmethyl chloroformate; an aromatic chloroformate having a condensation ring structure such as naphthalene chloroformate and tetralin chloroformate; and derivatives of these.

Examples of the alicyclic monochloroformate used as the reactive hydrocarbon compound include an alicyclic monochloroformate having a chloroformate group introduced in an alicycle, such as cyclopentyl chloroformate, cyclohexyl chloroformate and cyclooctyl chloroformate; an alicyclic monochloroformate having an aliphatic chloroformate group introduced in an alicycle such as cyclohexylmethyl chloroformate; and derivatives of these.

If an organic silicon compound and an organic fluorine compound are added to these reactive hydrocarbon compound structures, properties such as water resistance can be more effectively improved.

As the reactive functional groups of these reactive hydrocarbon compounds, any reactive functional groups are used as long as they can react with a hydroxy group of cellulose. Examples thereof include a carboxyl group, a carboxylic acid halide group (particularly, a carboxylic acid chloride group), a carboxylic acid anhydride, an isocyanate group, a chloroformate group and further include an epoxy group and a halogen group (particularly, a chloride group). Of these, a carboxyl group, a carboxylic halide group, an isocyanate group and a chloroformate group are preferable, and a car-

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boxylic acid chloride group, an isocyanate group and a chloroformate group are particularly preferable. As the carboxylic acid halide group (particularly, a carboxylic acid chloride group), an acid halide group (particularly, an acid chloride group) in which a carboxyl group of each of the carboxylic acids mentioned above is acid-halogenated, is mentioned.

As the reactive hydrocarbon compound used in the exemplary embodiment, particularly in view of rigidity (bending strength, etc.) of a resin, at least one monocarboxylic acid selected from aromatic carboxylic acids and alicyclic carboxylic acids, an acid halide or acid anhydride thereof, aromatic monoisocyanate, aliphatic monoisocyanate, aromatic monochloroformate and aliphatic monochloroformate are preferable. By adding such a reactive hydrocarbon compound to a hydroxy group of cellulose, a structure in which an acyl group derived from at least one type of monocarboxylic acid selected from aromatic carboxylic acids and alicyclic carboxylic acids, a carbamoyl group derived from at least one type of monoisocyanate selected from aromatic monoisocyanates and alicyclic monoisocyanates, or a carbonate group derived from at least one type of chloroformate selected from aromatic monochloroformates and alicyclic monochloroformates is added to the hydroxy group of cellulose, (more specifically, the structure formed by substituting the hydrogen atom of a hydroxy group of cellulose with an acyl group, a carbamoyl group or a carbonate group) can be obtained.

The number (average value) of reactive hydrocarbon compounds (the number of acyl groups, carbamoyl groups or carbonate groups, DS_{xx}) to be added per glucose unit of cellulose (or a derivative thereof), in other words, the number of hydroxy groups bound to a reactive hydrocarbon compound (the degree of substitution of the hydroxy group) (average value) is, in view of obtaining a desired effect, preferably 0.1 or more and 0.6 or less and more preferably 0.1 or more and 0.5 or less.

Furthermore, after cardanol (or a derivative thereof) and a reactive hydrocarbon compound are grafted, the number of remaining hydroxy groups (hydroxy group remaining degree, DS_{OH}) (average value) per glucose unit is, in view of sufficiently ensuring water resistance, preferably 0.9 or less and more preferably, 0.7 or less.

The reactive hydrocarbon compound can be grafted in the grafting step of cardanol (or a derivative thereof). Owing to this, grafting can be made uniformly. At this time, these may be added simultaneously or separately. However, if cardanol (or a derivative thereof) is grafted and thereafter a reactive hydrocarbon compound is added and grafted, the efficiency of a grafting reaction can be improved.

[Grafting Treatment]

A grafting treatment can be performed by heating cellulose (or a derivative thereof) and cardanol (or a derivative thereof), if necessary, a reactive hydrocarbon compound in a solvent dissolving them, at an appropriate temperature. Cellulose is rarely dissolved in a general solvent; however dissolved in e.g., a dimethylsulfoxide-amine solvent, a dimethylformamide-chloral-pyridine solvent, a dimethylacetamide-lithium chloride solvent and an imidazolium ionic liquid. When a grafting reaction is performed in a general solvent, a cellulose derivative, the solubility of which has been changed by previously binding a carboxylic acid and an alcohol to a part of hydroxy groups of cellulose to reduce intermolecular force, can be used. Acylated cellulose having a hydroxy group whose hydrogen atom is substituted with an acyl group such as an acetyl group, a propionyl group and a butyryl group is preferable. In particular, cellulose acetate, which is a cellulose acetylated by acetic acid or acetyl chloride is preferable. Acetic acid, propionic acid, butyric acid and an acid halide

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and acid anhydride thereof are included in the aforementioned reactive hydrocarbon compounds; however, like this example, whole or part of predetermined reactive hydrocarbon compounds can be added (grafted) to a hydroxy group of cellulose before grafting with cardanol (or a derivative thereof).

[Remaining Amount of Hydroxy Group]

The remaining hydroxy group that is not used in grafting cardanol (or a derivative thereof) is a hydroxy group without being modified, a modified hydroxy group by acetylation, or a hydroxy group to which a reactive hydrocarbon compound is added (grafted). As the amount of hydroxy group increases, maximum strength and heat resistance tend to increase; whereas water absorbability tends to increase. As the conversion rate (degree of substitution) of hydroxy groups increases, water absorbability tends to decrease, plasticity and breaking strain tend to increase; whereas, maximum strength and heat resistance tend to decrease. In consideration of these tendencies and grafting conditions, the conversion rate of hydroxy groups can be appropriately set.

In view of ensuring sufficient water resistance, the number of remaining hydroxy groups of a cellulose resin grafted per glucose unit (hydroxy group remaining degree, DS_{OH}) (average value) is preferably 0.9 or less and more preferably 0.7 or less.

[Degree of Substitution of the Hydroxyl Group by Acylation]

In view of water absorbability, mechanical strength and heat resistance, it is preferred that the hydroxy groups of cellulose are partly acylated with a reactive hydrocarbon as mentioned above. Furthermore, in view of the aforementioned grafting treatment of cardanol (or a derivative thereof), it is preferred that hydroxy groups of cellulose are appropriately acylated (particularly, acetylated) before grafting of cardanol (or a derivative thereof). The number (average value) of acyl groups to be added per glucose unit of cellulose (or a derivative thereof), in other words, the number of hydroxy groups acylated (degree of substitution of the hydroxy group, DS_{AC}) (average value) is preferably 0.5 or more in view of obtaining sufficient acylation effect, more preferably 1.0 or more, and further preferably 1.5 or more. Furthermore, in view of ensuring the sufficient grafting rate (DS_{CD}) of cardanol (or a derivative thereof), the degree of substitution of the hydroxy group, DS_{AC} by acylation is preferably 2.7 or less, more preferably 2.5 or less and further preferably 2.2 or less. The acyl group to be added by acylation is preferably at least one acyl group selected from an acetyl group, a propionyl group and a butyryl group. Note that the degree of substitution by acetylation is represented by DS_{Ace} , the degree of substitution by propionation is represented by DS_{Pr} , and the degree of substitution by butylation is represented by DS_{Bu} .

[Plant Component Ratio]

In the cellulose resin according to the exemplary embodiment, in view of ensuring a sufficient plant utilization ratio, the mass ratio of the sum of a cellulose component and a cardanol component relative to the total cellulose resin after grafting (plant component ratio) is preferably 50% or more and more preferably 60% or more. Herein, the cellulose component corresponds to the structure represented by Formula (1) where the hydroxy groups are not acylated or grafted, whereas the cardanol component corresponds to the structure represented by Formula (2). On the assumption of these, calculation is made.

[Additives]

To the cellulose resin according to the exemplary embodiment described above, various types of additives usually used in thermoplastic resins can be applied. For example, if a

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plasticizer is added, thermoplasticity and breaking elongation can be more improved. Examples of such a plasticizer include phthalic esters such as dibutyl phthalate, diaryl phthalate, diethyl phthalate, dimethyl phthalate, di-2-methoxyethyl phthalate, ethyl phthalyl ethyl glycolate and methyl phthalyl ethyl glycolate; tartaric acid esters such as dibutyl tartrate; adipic acid esters such as dioctyl adipate and diisononyl adipate; polyhydric alcohol esters such as triacetin, diacetyl glycerin, tripropionitrile glycerin and glyceryl monostearate; phosphoric acid esters such as triethyl phosphate, triphenyl phosphate and tricresyl phosphate; dibasic fatty acid esters such as dibutyl adipate, dioctyl adipate, dibutyl azelate, dioctyl azelate and dioctyl sebacate; citric acid esters such as triethyl citrate, acetyltriethyl citrate and tributyl acetyl citrate; epoxylated vegetable oils such as epoxylated soybean oil and epoxylated linseed oil; castor oil and a derivative thereof; benzoic acid esters such as ethyl O-benzoyl benzoate; aliphatic dicarboxylic acid esters such as sebacate and azelate; unsaturated dicarboxylic acid esters such as maleate; and N-ethyl toluene sulfonamide, triacetin, O-cresyl p-toluene-sulfonate and tripropionin.

Examples of other plasticizers include cyclohexane dicarboxylic acid esters such as dihexyl cyclohexanedicarboxylate, dioctyl cyclohexanedicarboxylate and di-2-methyloctyl cyclohexanedicarboxylate; trimellitic acid esters such as dihexyl trimellitate, diethylhexyl trimellitate and dioctyl trimellitate; and pyromellitic acid esters such as dihexyl pyromellitate, diethylhexyl pyromellitate and dioctyl pyromellitate.

The reactive functional group (a carboxylic acid group, a group derived from a carboxylic acid group, other functional groups) of such a plasticizer may be reacted with a hydroxy group or an unsaturated bond of cardanol to allow cardanol to add to a plasticizer. If such a plasticizer is used, compatibility of the cellulose resin of the exemplary embodiment and the plasticizer can be improved. Therefore, the addition effect of the plasticizer can be more improved.

To the cellulose resin of the exemplary embodiment, if necessary, an inorganic or organic granular or fibrous filler can be added. By adding a filler, strength and rigidity can be more improved. Examples of the filler include, mineral particles (talc, mica, baked siliceous earth, kaolin, sericite, bentonite, smectite, clay, silica, quartz powder, glass beads, glass powder, glass flake, milled fiber, Wollastonite, etc.), boron-containing compounds (boron nitride, boron carbonate, titanium boride etc.), metal carbonates (magnesium carbonate, heavy calcium carbonate, light calcium carbonate, etc.), metal silicates (calcium silicate, aluminum silicate, magnesium silicate, magnesium aluminosilicate, etc.), metal oxides (magnesium oxide etc.), metal hydroxides (aluminum hydroxide, calcium hydroxide, magnesium hydroxide, etc.), metal sulfates (calcium sulfate, barium sulfate, etc.), metal carbides (silicon carbide, aluminum carbide, titanium carbide, etc.), metal nitrides (aluminum nitride, silicon nitride, titanium nitride, etc.), white carbon and metal foils. Examples of the fibrous filler include organic fibers (natural fiber, papers etc.), inorganic fibers (glass fiber, asbestos fiber, carbon fiber, silica fiber, silica alumina fiber, Wollastonite, zirconia fiber, potassium titanate fiber etc.) and metal fibers. These fillers can be used singly or in combination of two or more types.

To the cellulose resin of the exemplary embodiment, if necessary, a flame retardant can be added. By adding a flame retardant, flame resistance can be imparted. Examples of the flame retardant include magnesium hydroxide, aluminum hydroxide, metal hydrates such as hydrotalcite, basic magnesium carbonate, calcium carbonate, silica, alumina, talc, clay, zeolite, bromine-based flame retardant, antimony trioxide, phosphoric acid based flame retardant (aromatic phosphate,

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aromatic condensed phosphate, etc.), compounds containing phosphorus and nitrogen (phosphazene compound), etc. These flame retardants can be used singly or in combination with two or more types.

Furthermore, as the flame retardant, a reaction product between a phosphorus oxide, a phosphoric acid or a derivative of each of these and cardanol, and a polymer of the reaction product can be used. If such a flame retardant is used, the interaction between the cellulose resin of the exemplary embodiment and a flame retardant is enhanced, excellent flame-retardant effect can be obtained. Examples of such a flame retardant include a reaction product between phosphorus oxide (P_2O_5) or phosphoric acid (H_3PO_4) and a hydroxy group of cardanol, and a polymer obtained by adding hexamethylene tetramine to the reaction product, followed by polymerizing.

To the cellulose resin of the exemplary embodiment, if necessary, an impact resistance improver can be added. By adding a impact resistance improver, impact resistance can be improved. Examples of the impact resistance improver include a rubber component and a silicone compound. Examples of the rubber component include a natural rubber, epoxylated natural rubber and synthesized rubber. Furthermore, examples of the silicone compound include organic polysiloxane formed by polymerization of alkyl siloxane, alkyl phenyl siloxane, etc., and modified silicone compounds obtained by modifying a side chain or an end of an organic polysiloxane as mentioned above with polyether, methylstyryl, alkyl, higher fatty acid ester, alkoxy, fluorine, an amino group, an epoxy group, a carboxyl group, a carbinol group, a methacryl group, a mercapto group, a phenol group etc. These impact resistance improvers can be used singly or in combination of two or more types.

As the silicone compound, a modified silicone compound (modified polysiloxane compound) is preferred. As the modified silicone compound, a modified polydimethyl siloxane is preferred, which has a structure having a main chain constituted of dimethyl siloxane repeat units and a side chain or a terminal methyl group partly substituted with an organic substituent containing at least one group selected from an amino group, an epoxy group, a carbinol group, a phenol group, a mercapto group, a carboxyl group, a methacryl group, a long-chain alkyl group, an aralkyl group, a phenyl group, a phenoxy group, an alkyl phenoxy group, a long-chain fatty acid ester group, a long-chain fatty acid amide group and a polyether group. The modified silicone compound, because of the presence of such an organic substituent, is improved in affinity for the aforementioned cardanol-added cellulose resin and dispersibility in the cellulose resin is improved. Consequently, a resin composition excellent in impact resistance can be obtained.

As such a modified silicone compound, a modified silicone compound produced in accordance with a conventional method can be used.

Examples of the organic substituent contained in the modified silicone compound include the organic substituents represented by the following formulas (3) to (21):

[Formula 3]



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-continued

[Formula 4]



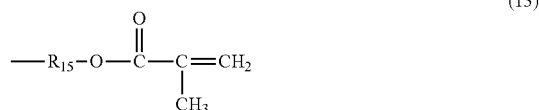
[Formula 5]



[Formula 6]



[Formula 7]



[Formula 8]



[Formula 9]



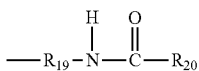
[Formula 10]



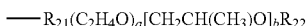
17

-continued

[Formula 11]



[Formula 12]



where a and b each represent an integer of 1 to 50.

In the aforementioned formulas, R_1 to R_{10} , R_{12} to R_{15} , R_{19} and R_{21} each represent an alkyl group having at most 20 carbon atoms. Examples of the divalent organic group include alkylene groups such as a methylene group, an ethylene group, a propylene group and a butylene group; alkyl arylene groups such as a phenylene group and a tolylene group; oxyalkylene groups and polyoxyalkylene groups such as $-(\text{CH}_2-\text{CH}_2-\text{O})_c-$ (c represents an integer from 1 to 50), and $-\text{[CH}_2-\text{CH}(\text{CH}_3)-\text{O}]_d-$ (d represents an integer from 1 to 50); and $-(\text{CH}_2)_n-\text{NHCO}-$ (e represents an integer from 1 to 8). Of these, an alkylene group is preferable and particularly, an ethylene group and a propylene group are preferable.

In the aforementioned formulas, R_{11} , R_{16} to R_{18} , R_{20} and R_{22} each represent an alkyl group having at most 20 carbon atoms. Examples of the alkyl group include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group and a pentadecyl group. Furthermore, the structures of the above alkyl groups may have one or more unsaturated bonds.

The total average content of organic substituents in a modified silicone compound desirably falls within the range where the modified silicone compound having an appropriate particle diameter (for example, 0.1 μm or more and 100 μm or less) can be dispersed in a matrix, i.e., a cardanol-added cellulose resin, during a process for producing a cellulose resin composition. If a modified silicone compound having an appropriate particle diameter is dispersed in a cardanol-added cellulose resin, stress concentration on the periphery of a silicone region having a low elastic modulus effectively occurs. As a result, a resin molded product having excellent impact resistance can be obtained. The total average content of such organic substituents is preferably 0.01% by mass or more and more preferably 0.1% by mass or more, and also preferably 70% by mass or less and more preferably 50% by mass or less. If an organic substituent is contained appropriately, the modified silicone compound can be improved in affinity for a cellulose resin, the modified silicone compound having an appropriate particle diameter can be dispersed in a cardanol-added cellulose resin, and further bleed out due to separation of the modified silicone compound in a molding can be suppressed. If the total average content of the organic substituents is excessively low, it becomes difficult to disperse a modified silicone compound having an appropriate particle diameter in a cardanol-added cellulose resin.

If an organic substituent of the modified polydimethyl siloxane compound is an amino group, an epoxy group, a carbinol group, a phenol group, a mercapto group, a carboxyl group or a methacryl group, the average content of the organic substituent in the modified polydimethyl siloxane compound can be obtained by the following Expression (I).

Organic substituent average content (%)=(organic substituent formula-weight/organic substituent equivalent) $\times 100$

(20)

(21)

from the following Expression (II).

Organic substituent average content (%)= $\frac{xw}{74+x(59+w)}\times 100$

(II)

In the Expression (II), x is an average molar fraction of the organic substituent-containing a siloxane repeat unit relative to all siloxane repeat units of the modified polydimethyl siloxane compound; and w is the formula weight of the organic substituent.

In the case where the organic substituent of the modified polydimethyl siloxane compound is a phenyl group, the average content of the phenyl group in the modified polydimethyl siloxane compound can be obtained by the following Expression (III).

Phenyl group average content (%)= $\frac{154x}{198x+74(1-x)}\times 100$

(III)

In the Expression (III), x is an average molar fraction of the phenyl group-containing siloxane repeat unit relative to all siloxane repeat units in the modified polydimethyl siloxane compound (A).

In the case where the organic substituent of the modified polydimethyl siloxane compound is a polyether group, the average content of the polyether group in the modified polydimethyl siloxane compound can be obtained by the following Expression (IV).

Polyether group average content (%)= $\frac{\text{HLB value}}{100}\times 20$

(IV)

In the Expression (IV), the HLB value represents the degree of affinity of a surfactant for water and oil, and is defined by the following Expression (V) based on the Griffin Act.

HLB value= $20\times \frac{\text{sum of formula weights of hydrophilic moieties}}{\text{molecular weight}}$

(V)

To the cellulose resin of the exemplary embodiment, two or more modified silicone compounds having different affinities to the resin may be added. In this case, dispersibility of a relative low-affinity modified silicone compound (A1) is improved by a relative high-affinity modified silicone compound (A2) to obtain a cellulose resin composition having even more excellent impact resistance. The total average content of an organic substituent of the relatively low-affinity modified silicone compound (A1) is preferably 0.01% by mass or more and more preferably 0.1% by mass or more and also preferably 15% by mass or less and more preferably 10% by mass or less. The total average content of an organic substituent of the relatively high-affinity modified silicone compound (A2) is preferably 15% by mass or more and more preferably 20% by mass or more and also preferably 90% by mass or less.

The blending ratio (mass ratio) of the modified silicone compound (A1) to the modified silicone compound (A2) can be set to fall within the range of 10/90 to 90/10.

In a modified silicone compound, dimethyl siloxane repeat units and organic substituent-containing siloxane repeat units each of which may be homologously and continuously con-

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nected, alternately connected or connected at random. A modified silicone compound may have a branched structure.

The number average molecular weight of a modified silicone compound is preferably 900 or more and more preferably 1000 or more, and also preferably 1000000 or less, more preferably 300000 or less and further preferably 100000 or less. If the molecular weight of a modified silicone compound is sufficiently large, loss by vaporization can be suppressed in kneading with a melted cellulose resin during a process for producing a cardanol-added cellulose resin compound. Furthermore, if the molecular weight of a modified silicone compound is appropriate (not excessively large), a uniform molding having good dispersibility can be obtained.

As the number average molecular weight, a value (calibrated by a polystyrene standard sample) obtained by measuring a 0.1% chloroform solution of a sample by GPC can be employed.

The addition amount of such a modified silicone compound is preferably, in view of obtaining sufficient addition effect, 1% by mass or more relative to the total cellulose resin composition and more preferably 2% by mass or more. In view of sufficiently ensuring properties of a cellulose resin such as strength and suppressing bleed out, the addition amount of a modified silicone compound is preferably 20% by mass or less and more preferably 10% by mass or less.

By adding such a modified silicone compound to a cellulose resin, the modified silicone compound having an appropriate particle diameter (for example, 0.1 to 100 μm) can be dispersed in the resin and the impact resistance of a resin composition can be improved.

As the impact resistance improver, a cardanol polymer containing cardanol as a main component may be used. Such an impact resistance improver has excellent compatibility with the cellulose resin of the exemplary embodiment and therefore a higher impact resistance improving effect can be obtained. Specific examples thereof include a cardanol polymer obtained by adding formaldehyde to cardanol and reacting this mixture with an unsaturated bond in the straight-chain hydrocarbon of cardanol; and a cardanol polymer obtained by adding a catalyst such as sulfuric acid, phosphoric acid or diethoxytrifluoroboron and reacting unsaturated bonds of the straight-chain hydrocarbon of cardanol with each other.

To the cellulose resin of the exemplary embodiment, if necessary, additives such as a colorant, an antioxidant and a heat stabilizer may be added as long as they are applied to conventional resin compositions.

To the cellulose resin of the exemplary embodiment, if necessary, a general thermoplastic resin may be added.

Particularly, by adding a thermoplastic resin having excellent flexibility such as a thermoplastic polyurethane elastomer (TPU), impact resistance can be improved. The addition amount of such a thermoplastic resin (particularly, TPU) is, in view of obtaining sufficient addition effect, preferably 1% by mass or more and more preferably 5% by mass or more relative to the total composition containing the cellulose resin of the exemplary embodiment. In view of ensuring the properties of a cellulose resin such as strength and suppressing bleed out, the addition amount of thermoplastic resin is preferably 20% by mass or less and more preferably 15% by mass or less.

The thermoplastic polyurethane elastomer (TPU) suitable for improving impact resistance that can be used includes a polyurethane elastomer prepared by from a polyol, a diisocyanate and a chain extender.

Examples of the polyol include polyester polyol, polyester ether polyol, polycarbonate polyol and polyether polyol.

Examples of the polyester polyol include a polyester polyol obtained by a dehydration condensation reaction between a polyvalent carboxylic acid such as an aliphatic dicarboxylic acid (succinic acid, adipic acid, sebacic acid, azelaic acid, etc.), an aromatic dicarboxylic acid (phthalic acid, terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, etc.), an alicyclic dicarboxylic acid (hexahydrophthalic acid, hexahydroterephthalic acid, hexahydroisophthalic acid, etc.), or an acid ester or an acid anhydride of each of these, and a polyol such as ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, neopentyl glycol, 1,3-octane diol, 1,9-nonane diol, or a mixture of these; and a polylactone diol obtained by ring-opening polymerization of a lactone monomer such as ϵ -caprolactone.

Examples of the polyester ether polyol include a compound obtained by a dehydration condensation reaction between a polyvalent carboxylic acid such as an aliphatic dicarboxylic acid (succinic acid, adipic acid, sebacic acid, azelaic acid, etc.), an aromatic dicarboxylic acid (phthalic acid, terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, etc.), an alicyclic dicarboxylic acid (hexahydrophthalic acid, hexahydroterephthalic acid, hexahydroisophthalic acid, etc.), or an acid ester or an acid anhydride of each of these, and a glycol such as diethylene glycol or an alkylene oxide adduct (propylene oxide adduct etc.) or a mixture of these.

Examples of the polycarbonate polyol include a polycarbonate polyol obtained by reacting one or two or more polyols such as ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, neopentyl glycol, 1,8-octane diol, 1,9-nonane diol and diethylene glycol with diethylene carbonate, dimethyl carbonate, diethyl carbonate, etc.; and further may include a copolymer of a polycaprolactone polyol (PCL) and a polyhexamethylene carbonate (PHL).

Examples of the polyether polyol include a polyethylene glycol, polypropylene glycol and polytetramethylene ether glycol, each of which is obtained by polymerizing respective cyclic ethers: ethylene oxide, propylene oxide and tetrahydrofuran; and copolyethers of these.

Examples of the diisocyanate to be used in formation of TPU include tolylene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthylene diisocyanate (NDI), tolidine diisocyanate, 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), xylylene diisocyanate (XDI), hydrogenated XDI, triisocyanate, tetramethyl xylene diisocyanate (TMXDI), 1,6,11-undecane triisocyanate, 1,8-diisocyanatemethyl octane, lysine ester triisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate and dicyclohexyl methane diisocyanate (hydrogenated MDI; HMDI). Of these, 4,4'-diphenylmethane diisocyanate (MDI) and 1,6-hexamethylene diisocyanate (HDI) are preferably used.

Examples of the chain extender to be used in formation of TPU, a low-molecular weight polyol can be used. Examples of the low-molecular weight polyol include aliphatic polyols such as ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, 3-methyl-1,5-pentane diol, neopentyl glycol, 1,8-octane diol, 1,9-nonane diol, diethylene glycol and 1,4-cyclohexane dimethanol and glycerin; and aromatic glycols such as 1,4-dimethylolbenzene, bisphenol A and ethylene oxide or a propylene oxide adduct of bisphenol A.

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When a silicone compound is copolymerized with a thermoplastic polyurethane elastomer (TPU) obtained from these materials, further excellent impact resistance can be obtained.

These thermoplastic polyurethane elastomers (TPU) may be used singly or in combination.

A method for producing a resin composition containing the cellulose resin of the exemplary embodiment, additives and a thermoplastic resin, is not particularly limited. For example, the resin composition can be produced by melting and mixing additives and the cellulose resin manually by handmixing or by use of a known mixer such as a tumbler mixer, a ribbon blender, a single-axial or a multiaxial mixing extruder, and a compounding apparatus such as a kneader and kneading roll and, if necessary, granulating the mixture into an appropriate shape. In another preferable process, additives dispersed in solvent such as an organic solvent and a resin are mixed and furthermore, if necessary, a coagulation solvent is added to obtain a mixed composition of the additives and the resin and thereafter, the solvent is evaporated.

The cellulose resin according to the exemplary embodiments mentioned above can be used as a base resin for a molding material. The molding material using the cellulose resin as a base resin is suitable for forming a molded article such as housing, e.g., packaging for an electronic device.

The base resin herein refers to a main component of the molding material and means that other components may be contained as long as the components do not prevent the function of the main component. The content rate of the main component is not particularly limited; however, the content rate of the main component in a composition is 50% by mass or more, preferably 70% by mass or more, more preferably 80% by mass or more and particularly preferably 90% by mass or more.

EXAMPLES

The present invention will be more specifically described by way of examples below.

Synthesis Example 1

Synthesis of Modified Cardanol 1 (Cardanol with a Chloroformate Group)

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics) prepared by hydrogenating an unsaturated bond of the straight-chain hydrocarbon moiety of the cardanol was used as a raw material. The phenolic hydroxy group of the hydrogenated cardanol was reacted with phosgen to obtain cardanol with a chloroformate group. More specifically, cardanol with a chloroformate group was prepared in accordance with the following procedure.

After hydrogenated cardanol (80 g (0.26 mol)) was dissolved in chlorobenzene (120 mL), phosgen was supplied for 5 hours at 100° C. while stirring the mixture. Thereafter, the solvent was distilled away under reduced pressure to obtain cardanol with a chloroformate group (96 g (0.26 mol)).

Synthesis Example 2

Synthesis of Modified Cardanol 2 (Cardanol with an Isocyanate Group)

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics) prepared by hydrogenating an unsaturated bond of the straight-chain hydrocarbon moiety of the cardanol was used as a raw material. The phenolic

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hydroxy group of the hydrogenated cardanol was reacted with sodium hydroxide and 2-bromoisobutylamide to add an amino group. In this manner, aminated and hydrogenated cardanol was obtained. Subsequently, the amino group was reacted with phosgen to convert the amino group to an isocyanate group. In this manner, cardanol with an isocyanate group was obtained. More specifically, cardanol with an isocyanate group was prepared in accordance with the following procedure.

Hydrogenated cardanol (91 g (0.30 mol)) was dissolved in dimethylformamide (450 mL), and sodium hydroxide (36 g (0.90 mol)) was added. After the solution was stirred at room temperature for one hour, 2-bromoisobutylamide (150 g (0.90 mol)) was added. The mixture was further stirred at room temperature for 3 hours. Thereafter, to the reaction solution, sodium hydroxide (108 g (2.7 mol)) was added, and the reaction solution was stirred at 50° C. for one hour. Then, water (450 mL) and sodium hydroxide (72 g (1.8 mol)) were further added, and the reaction solution was refluxed at 100° C. for one hour. After completion of the reaction, water (900 mL) was added and the solution was cooled to room temperature. The precipitated solid substance was separated by filtration, dried in air overnight and further dried under vacuum at 105° C. for 5 hours to obtain aminated and hydrogenated cardanol (78 g).

The obtained aminated and hydrogenated cardanol (78 g (0.26 mol)) was dissolved in chlorobenzene (120 mL), and then, phosgen was supplied for 2 hours at 80° C. while stirring. Thereafter, the solvent was distilled away under reduced pressure to obtain cardanol with an isocyanate group (96 g (0.26 mol)).

Synthesis Example 3

Synthesis of Chloridized and Monochloro Acetic Acid Modified Cardanol (Chloridized and Hydrogenated Cardanol) (Corresponding to Reference Synthesis Example 2 (Described Later))

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics), in which an unsaturated bond of the straight-chain hydrocarbon moiety of cardanol is hydrogenated, was used as a raw material. The phenolic hydroxy group of the hydrogenated cardanol was reacted with monochloro acetic acid to add a carboxyl group to obtain carboxylated and hydrogenated cardanol. Subsequently, the carboxyl group was converted into an acid chloride group by chloridizing with oxalyl chloride to obtain chloridized and hydrogenated cardanol. More specifically, the chloridized and hydrogenated cardanol was prepared in accordance with the following procedure.

First, hydrogenated cardanol (80 g (0.26 mol)) was dissolved in methanol (120 mL). To this, an aqueous solution of sodium hydroxide (64 g (1.6 mol)) dissolved in distilled water (40 mL) was added. Thereafter, a solution of monochloro acetic acid (66 g (0.70 mol)) manufactured by Kanto Chemical Co., Inc. dissolved in methanol (50 mL) was added dropwise at room temperature. After completion of dropwise addition, stiffing was continued while refluxing at 73° C. for 4 hours. After the reaction solution was cooled to room temperature, the reaction mixture was acidified with a diluted hydrochloric acid until pH became 1. To this, methanol (250 mL) and diethyl ether (500 mL) and further distilled water (200 mL) were added. The resultant water layer was separated by a separating funnel and discarded. The resultant ether layer was washed twice with distilled water (400 mL). To the ether layer, magnesium anhydride was added to dry the ether layer,

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which was then separated by filtration. The filtrate (ether layer) was concentrated by an evaporator (90° C./3 mmHg) under reduced pressure to obtain a yellow brown powdery crude product as the residue. The crude product was recrystallized from n-hexane and dried under vacuum to obtain a white powder of carboxylated and hydrogenated cardanol (46 g (0.12 mol)).

The carboxylated and hydrogenated cardanol (46 g (0.12 mol)) thus obtained was dissolved in dehydrated chloroform (250 mL). To this, oxalyl chloride (24 g (0.19 mol)) and N, N-dimethylformamide (0.25 mL (3.2 mmol)) were added. The mixture was stirred for 72 hours at room temperature. Chloroform, excessive oxalyl chloride and N,N-dimethylformamide were distilled away under reduced pressure to obtain chloridized and hydrogenated cardanol (48 g (0.13 mol)).

Example 1

Cardanol with a chloroformate group prepared in Synthesis Example 1 was allowed to bind to cellulose acetate (trade name: LM-80 manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of substitution by acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10.0 g (the amount of hydroxy group: 0.040 mol)) was dissolved in dehydrated pyridine (500 mL). This solution was ice cooled. To this, a dioxane solution (60 mL) dissolving cardanol with a chloroformate group (8.5 g (0.023 mol)) prepared in Synthesis Example 1 was gently added and stirred under room temperature for one hour. The reaction solution was gently added dropwise to methanol (6 L) while stirring to reprecipitate a solid substance. The solid substance was separated by filtration, dried overnight in air and further dried at 105° C. for 5 hours under vacuum to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.43.

The process chart from raw-material cardanol until the sample is obtained (Synthesis Example 1→Example 1) is shown in FIG. 1.

Furthermore, the sample was evaluated in accordance with the following procedure. The results are shown in Table 1. [Evaluation of Thermoplasticity (Press Moldability)]

Press molding was performed in the following conditions to obtain a molded product. At that time, moldability was evaluated in accordance with the following criteria. (Molding Conditions)

Temperature: 200° C., Time: 2 minutes, Pressure: 100 kgf (9.8×10² N),

Size of molded product: Thickness: 2 mm, Width: 13 mm, Length: 80 mm.

(Evaluation Criteria)

○: Good, Δ: not good (void, sink mark or partial uncharged portion was observed), x: cannot be molded.

[Measurement of Glass Transition Temperature (Heat Resistance Evaluation)]

Glass transition temperature was measured by DSC (product name: DSC6200, manufactured by Seiko Instruments Inc.).

[Bending Test]

The compact obtained by the aforementioned molding process was subjected to a bending test in accordance with JIS K7171.

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[Measurement of Water Absorption Rate]

Water absorption rate was measured in accordance with JIS K7209.

[Determination of Plant-Component Ratio]

A cellulose component and a cardanol component were regarded as plant components. The total content rate (% by mass) of the plant components relative to the whole sample was obtained. Assuming that the cellulose component herein corresponds to that having a structure represented by Formula (1) above in which a hydroxy group is not acylated or grafted, and that the cardanol component corresponds to that having a structure represented by Formula (2) above, calculation was made.

Example 2

Cardanol with isocyanate group prepared in Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of substitution by acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10.0 g (hydroxy-group amount: 0.040 mol)) was dissolved in dehydrated dioxane (200 mL), and dibutyl tin dilaurate (0.1 g) was added as a reaction catalyst. To the solution, a dioxane solution (100 mL) dissolving cardanol with isocyanate group (7.6 g (0.023 mol)) prepared in Synthesis Example 2 was added. The reaction solution was heated to reflux at 80° C. for 10 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.44.

The process chart from raw-material cardanol until the sample is obtained (Synthesis Example 2→Example 2) is shown in FIG. 2.

Furthermore, the sample was evaluated in accordance with the same manner as in Example 1. The results are shown in Table 1.

Reference Example 101

Corresponding to Reference Example 5 Described Later

Chloridized and hydrogenated cardanol prepared in Synthesis Example 3 (Reference Synthesis Example 2) was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd. (the number of acetic acid molecules added to a single glucose unit of cellulose (degree of substitution by acetylation: $DS_{Ace}=2.1$)) to obtain grafted cellulose acetate. More specifically, grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (amount of hydroxy group: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL), and triethylamine (5.0 mL (0.036 mol)) was added as a reaction catalyst and an acid-trapping agent. To this solution, a dioxane solution (100 mL) dissolving chloridized and hydrogenated cardanol (12 g (0.031 mol)) prepared in Reference Synthesis Example 2 was added and heated to reflux at 100°

C. for 3 hours. The reaction solution was gently added dropwise to methanol (3 L) while stirring to reprecipitate a solid substance. The solid substance was separated by filtration, dried overnight in air and further dried at 105° C. for 5 hours under vacuum to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.44.

The process chart from raw-material cardanol until the sample is obtained (Synthesis Example 3→Reference Example 101) is shown in FIG. 3.

Furthermore, the sample was evaluated in accordance with the same method as in Example 1. The results are shown in Table 1.

TABLE 1

		Example 1	Example 2	Reference Example 101
Amount of acetyl group	DS _{Ace} Mass fraction (%)	2.1 23	2.1 23	2.1 23
Amount of cardanol derivative	DS _{CD} modified with chloroformate	0.43	0	0
	DS _{CD} modified with isocyanate	0	0.44	0
	DS _{CD} modified with monochloro acetic acid-acid chloridized	0	0	0.44
	Mass fraction (%)	36	37	38
Addition amount of plasticizer [% by mass]		0	0	0
Bending strength [MPa]		73	72	60
Bending elasticity [GPa]		1.9	1.8	1.4
Bend-breaking strain [%]		>10	>10	>10
Glass transition temperature [° C.] (heat resistance)		148	147	142
Thermoplasticity (press moldability)		○	○	○
Water absorption rate [%]		1.3	1.3	1.3
Plant component ratio [%]		73	74	72

Apparently from comparison of Example 1 (cardanol added cellulose resin prepared by adding a cardanol derivative via a carbonate bond) and Example 2 (cardanol added cellulose resin prepared by adding a cardanol derivative via a urethane bond) with Reference Example 101 (cardanol added cellulose resin prepared by adding a cardanol derivative via an organic linking group derived from monochloroacetic acid), it was found that the cardanol added cellulose resins of Examples 1 and 2 are improved in strength, elastic modulus and heat resistance (T_g) while maintaining satisfactory bend-breaking strain and water resistance.

Apparently from the process charts shown in FIG. 1, FIG. 2 and FIG. 3, it is found that the cardanol added cellulose resins of Examples 1 and 2 can be easily produced in fewer steps than the cardanol added cellulose resin of Reference Example 101 with less amount of by-product.

Now, cardanol added cellulose resins to which a cardanol derivative is bound via a different organic linking group will be further specifically described by way of specific examples.

Reference Synthesis Example 1

Cardanol Derivative 1 (Preparation of Chloridized and Succinic Acid-Modified Cardanol)

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics), in which an unsaturated bond(s) of the straight-chain hydrocarbon moiety of cardanol are

hydrogenated, was used as a raw material. When the hydrogenated cardanol was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), no unsaturated bond was detected. Thus, it was confirmed that a hydrogenation rate is at least 90% by mole or more. The phenolic hydroxy group of the cardanol was reacted with succinic anhydride to add a carboxyl group to obtain carboxylated and hydrogenated cardanol. Next, the carboxyl group was converted into an acid chloride group by chloridizing it with oxalyl chloride to obtain chloridized and hydrogenated cardanol. More specifically, the chloridized and hydrogenated cardanol was prepared in accordance with the following procedure.

First, succinic anhydride (33 g (0.33 mol)) was dissolved in dehydrated chloroform (250 mL). To this, dehydrated pyridine (5.0 mL (0.062 mol)) and a raw material, i.e., hydrogenated cardanol (50 g (0.16 mol)) were added. The reaction solution was heated to reflux under a nitrogen atmosphere at 70° C. for 24 hours, cooled to room temperature. Thereafter, a crystal of succinic anhydride precipitated was separated by filtration. The chloroform solution filtrated was washed twice with 0.1 mol/L hydrochloric acid (250 mL) and further washed twice with water (250 mL). After washing, the chloroform solution was dehydrated with magnesium sulfate and magnesium sulfate was separated by filtration and chloroform was distilled away under reduced pressure to obtain a brown solid substance of carboxylated and hydrogenated cardanol (60 g (0.15 mol)).

The resultant carboxylated and hydrogenated cardanol (50 g (0.12 mol)) was dissolved in dehydrated chloroform (250 mL). To this, oxalyl chloride (24 g (0.19 mol)) and N,N-dimethylformamide (0.25 mL (3.2 mmol)) were added. The reaction solution was stirred at room temperature for 72 hours. Chloroform, excessive oxalyl chloride and N,N-dimethylformamide were distilled away under reduced pressure to obtain chloridized and hydrogenated cardanol (52 g (0.12 mol)).

Reference Synthesis Example 2

Cardanol Derivative 2 (Preparation of Chloridized and Monochloroacetic Acid-Modified Cardanol)

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics), in which an unsaturated bond(s) of the straight-chain hydrocarbon moiety of cardanol are hydrogenated, was used as a raw material. The phenolic hydroxy group of the cardanol was reacted with monochloroacetic acid to add a carboxyl group to obtain carboxylated and hydrogenated cardanol. Next, the carboxyl group was converted into an acid chloride group by chloridizing it with oxalyl chloride to obtain chloridized and hydrogenated cardanol. More specifically, the chloridized and hydrogenated cardanol was prepared in accordance with the following procedure.

First, hydrogenated cardanol (80 g (0.26 mol)) was dissolved in methanol (120 mL). To this, an aqueous solution of sodium hydroxide (64 g (1.6 mol)) dissolved in distilled water (40 mL) was added. Thereafter, at room temperature, a solution of monochloro acetic acid (66 g (0.70 mol)) (manufactured by Kanto Chemical Co., Inc.) dissolved in methanol (50 mL) was added dropwise. After completion of the dropwise addition, the reaction solution was continuously stirred while refluxing at 73° C. for 4 hours. The reaction solution was cooled to room temperature and the reaction mixture was acidified with a diluted hydrochloric acid until pH became 1. To this, methanol (250 mL) and diethyl ether (500 mL) and

further distilled water (200 mL) were added. The resultant water layer was separated by a separating funnel and discarded. The ether layer was washed twice with distilled water (400 mL). To the ether layer, magnesium anhydride was added to dry the ether layer and then separated by filtration. The filtrate (ether layer) was concentrated by an evaporator (90° C./3 mmHg) under reduced pressure to obtain a yellow brown powdery crude product as the residue. The crude product was recrystallized from n-hexane and dried under vacuum to obtain white powder of carboxylated and hydrogenated cardanol (46 g (0.12 mol)).

The resultant carboxylated and hydrogenated cardanol (46 g (0.12 mol)) was dissolved in dehydrated chloroform (250 mL). To this, oxalyl chloride (24 g (0.19 mol)) and N,N-dimethylformamide (0.25 mL (3.2 mmol)) were added. The mixture was stirred at room temperature for 72 hours. Chloroform, excessive oxalyl chloride and N,N-dimethylformamide were distilled away under reduced pressure to obtain chloridized and hydrogenated cardanol (48 g (0.13 mol)).

Reference Synthesis Example 3

Preparation of Biphenylacetyl Chloride

Biphenylacetic acid (6.0 g (0.028 mol)) manufactured by Sigma-Aldrich Co. LLC was dissolved in dehydrated chloroform (60 mL). To this, oxalyl chloride (3.7 g (0.029 mol)) and N,N-dimethylformamide (0.04 mL (0.51 mmol)) were added. The mixture was stirred at room temperature for 72 hours. Chloroform, excessive oxalyl chloride and N,N-dimethylformamide were distilled away under reduced pressure to obtain biphenylacetyl chloride (6.5 g (0.028 mol)).

Reference Example 1

The chloridized and hydrogenated cardanol (cardanol derivative 1) prepared in Reference Synthesis Example 1 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 mL (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (46 g (0.11 mol)) prepared in Reference Synthesis Example 1 was added. The reaction solution was heated to reflux at 100° C. for 6 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (20 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.90.

Furthermore, the sample was evaluated in the following procedure. The results are shown in Table 101A. [Evaluation of Thermoplasticity (Press Moldability)]

Press molding was performed in the following conditions to obtain a molded product. At that time, moldability was evaluated in accordance with the following criteria.

(Molding Conditions)

Temperature: 170° C., Time: 2 minutes, Pressure: 100 kgf (9.8×10² N),

Size of molded product: Thickness: 2 mm, Width: 13 mm, Length: 80 mm.

(Evaluation Criteria)

○: Good, Δ: not good (void, sink mark or partial uncharged portion was observed), x: cannot be molded.

[Measurement of Glass Transition Temperature (Heat Resistance Evaluation)]

Glass transition temperature was measured by DSC (product name: DSC6200, manufactured by Seiko Instruments Inc.).

[Bending Test]

The molded product obtained by the aforementioned molding process was subjected to a bending test in accordance with JIS K7171.

[Tensile Test]

A solution of a sample (2 g) dissolved in chloroform (20 mL) was prepared. The solution was subjected to casting and a film of 10 mm in width, 60 mm in length and 0.2 mm in thickness was prepared by cutting out by a cutter knife. The film was subjected to a tensile test in accordance with JIS K7127.

[Measurement of Water Absorption Rate]

Water absorption rate was obtained by measurement in accordance with JIS K7209.

[Determination of Plant-Component Ratio]

A cellulose component and a cardanol component were regarded as plant components. The total content rate (% by mass) of the plant components relative to the whole sample was obtained. Assuming that the cellulose component herein corresponds to that having a structure represented by Formula (1) above in which a hydroxy group is not acylated or grafted, and that the cardanol component corresponds to that having a structure represented by Formula (2) above, calculation was made.

Reference Example 2

The chloridized and hydrogenated cardanol (cardanol derivative 1) prepared in Reference Synthesis Example 1 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 mL (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (23 g (0.054 mol)) prepared in Reference Synthesis Example 1 was added. The reaction solution was heated to reflux at 100° C. for 6 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (16 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.55.

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Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101A.

Reference Example 3

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (14 g (0.037 mol)) prepared in Reference Synthesis Example 2 was added. The reaction solution was heated to reflux at 100° C. for 3 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (15 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.55.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101A.

Reference Example 4

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 3 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 21 g (0.054 mol) to obtain grafted cellulose acetate (19 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.80.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101A.

Reference Example 5

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 3 except that the supply amount of chlo-

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ridized and hydrogenated cardanol was changed to 12 g (0.031 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.44.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101A.

Reference Example 6

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 3 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 6.9 g (0.018 mol) to obtain grafted cellulose acetate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.30.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101A.

Reference Example 7

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: $DS_{Ace}=2.1$) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (4.1 g (0.011 mol)) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) (2.8 g (0.020 mol)) manufactured by Tokyo Kasei Kogyo Co., Ltd. was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.30 and DS_{BC} was 0.14.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 8

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were

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allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 7 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 3.1 g (0.008 mol) and the supply amount of benzoyl chloride was changed to 8.4 g (0.060 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by $^1\text{H-NMR}$ (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.22 and DS_{BC} was 0.27.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 9

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 7 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 7.6 g (0.020 mol) and the supply amount of benzoyl chloride was changed to 8.4 g (0.060 mol) to obtain grafted cellulose acetate (16 g).

The obtained sample (grafted cellulose acetate) was measured by $^1\text{H-NMR}$ (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.44 and DS_{BC} was 0.22.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 10

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 7 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 4.1 g (0.011 mol) and the supply amount of benzoyl chloride was changed to 28.1 g (0.20 mol) to obtain grafted cellulose acetate (15 g).

The obtained sample (grafted cellulose acetate) was measured by $^1\text{H-NMR}$ (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.24 and DS_{BC} was 0.42.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 11

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and

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benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 7 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 4.6 g (0.012 mol) and the supply amount of benzoyl chloride was changed to 1.1 g (0.008 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by $^1\text{H-NMR}$ (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.30 and DS_{BC} was 0.07.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 12

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 7 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 1.5 g (0.004 mol) and the supply amount of benzoyl chloride was changed to 2.2 g (0.016 mol) to obtain grafted cellulose acetate (12 g).

The obtained sample (grafted cellulose acetate) was measured by $^1\text{H-NMR}$ (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.08 and DS_{BC} was 0.16.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 13

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and biphenylacetyl chloride (BAA) prepared in Reference Synthesis Example 3 as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (7.0 g (0.018 mol)) prepared in Reference Synthesis Example 2 and biphenylacetyl chloride (BAA) (1.5 g (0.0065 mol)) prepared in Reference Synthesis Example 3 was added. The reaction solution was heated to reflux at 100°C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration,

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dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.27 and DS_{BAA} was 0.15.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 14

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and biphenylacetyl chloride (BAA) prepared in Reference Synthesis Example 3 as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 13 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 12.2 g (0.032 mol) and the supply amount of biphenylacetyl chloride was changed to 4.6 g (0.020 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.40 and DS_{BAA} was 0.40.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 15

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and biphenylacetyl chloride (BAA) prepared in Reference Synthesis Example 3 as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 13 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 15.2 g (0.040 mol) and the supply amount of biphenylacetyl chloride was changed to 3.2 g (0.014 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.55 and DS_{BAA} was 0.28.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 16

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and biphenylacetyl chloride (BAA) prepared in Reference Synthesis Example 3 as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose

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acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 13 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 7.6 g (0.020 mol) and the supply amount of biphenylacetyl chloride was changed to 7.4 g (0.032 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.30 and DS_{BAA} was 0.52.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101B.

Reference Example 17

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and phenylpropionyl chloride (PPA) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (4.0 g (0.011 mol)) prepared in Reference Synthesis Example 2 and phenylpropionyl chloride (PPA) (2.0 g (0.012 mol)) manufactured by Tokyo Kasei Kogyo Co., Ltd. was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.17 and DS_{PPA} was 0.25.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Reference Example 18

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and phenylpropionyl chloride (PPA) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, preparation was made in accordance with the same content and manner as in Reference Example 17 except that the supply amount of the chloridized and hydrogenated cardanol was changed to 3.8 g (0.010 mol) and the supply amount of phenylpropionyl chloride was changed to 2.7 g (0.016 mol) to obtain grafted cellulose acetate (14 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.13 and DS_{PPA} was 0.35.

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Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Reference Example 19

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and cyclohexanecarboxylic acid chloride (CHC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (3.7 g (0.0096 mol)) prepared in Reference Synthesis Example 2 and cyclohexanecarboxylic acid chloride (CHC) (2.5 g (0.017 mol)) manufactured by Sigma-Aldrich Co. LLC was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.20 and DS_{CHC} was 0.22.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Reference Example 20

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and biphenylcarbonyl chloride (BCC) as a reactive hydrocarbon were allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (4.6 g (0.012 mol)) prepared in Reference Synthesis Example 2 and biphenylcarbonyl chloride (BCC) (13.0 g (0.060 mol)) manufactured by Sigma-Aldrich Co. LLC was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (16 g).

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The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.30 and DS_{BCC} was 0.30.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Reference Example 21

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: LM-40, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.4) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (15.8 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (6.8 g (0.018 mol)) prepared in Reference Synthesis Example 2 was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (19 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.19.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 102.

Reference Example 22

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate (trade name: L-40, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.4) to obtain grafted cellulose acetate. More specifically, grafted cellulose acetate (25 g) was prepared in accordance with the same content and manner as in Reference Example 21 except that the supply amount of chloridized and hydrogenated cardanol was changed to 41.2 g (0.108 mol).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.50.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 102.

Reference Example 23

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate butyrate (trade name: CAB-381-20, manufactured by Eastman Chemical Company, the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=1.0; the number of butyric acid molecules added to a single glu-

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cose unit of cellulose (degree of butyration: DS_{Bu})=1.66) to obtain grafted cellulose acetate butyrate. More specifically, the grafted cellulose acetate butyrate was prepared in accordance with the following procedure.

Cellulose acetate butyrate (10 g (hydroxy-group amount: 0.011 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (2.5 ml (0.018 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (13 g (0.035 mol)) prepared in Reference Synthesis Example 2 was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate butyrate (13 g).

The obtained sample (grafted cellulose acetate butyrate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.34.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Reference Example 24

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 was allowed to bind to cellulose acetate propionate (trade name: CAP-482-20, manufactured by Eastman Chemical Company, the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=0.18; the number of propionic acid molecules added to a single glucose unit of cellulose (degree of propionation: DS_{Pr})=2.49) to obtain grafted cellulose acetate propionate. More specifically, the grafted cellulose acetate propionate was prepared in accordance with the following procedure.

Cellulose acetate propionate (10 g (hydroxy-group amount: 0.010 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (2.5 ml (0.018 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (13 g (0.035 mol)) prepared in Reference Synthesis Example 2 was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate propionate (13 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.34.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Reference Example 25

The chloridized and hydrogenated cardanol (cardanol derivative 2) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) as a reactive hydrocarbon were allowed to bind to cellulose acetate propionate (trade name: CAP-482-20, manufactured by Eastman Chemical Company, the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=0.18; the number of propionic acid molecules added to a single glucose

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unit of cellulose (degree of propionation: DS_{Pr})=2.49) to obtain grafted cellulose acetate propionate. More specifically, the grafted cellulose acetate propionate was prepared in accordance with the following procedure.

Cellulose acetate propionate (10 g (hydroxy-group amount: 0.010 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (2.5 ml (0.018 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving the chloridized and hydrogenated cardanol (4.5 g (0.012 mol)) prepared in Reference Synthesis Example 2 and benzoyl chloride (BC) (2.8 g (0.020 mol)) manufactured by Tokyo Kasei Kogyo Co., Ltd. was added. The reaction solution was heated to reflux at 100° C. for 5 hours. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate propionate (13 g).

The obtained sample (grafted cellulose acetate propionate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{CD} was 0.21 and DS_{BC} was 0.10.

Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Reference Example 26

Hydrogenated cardanol (m-n-pentadecylphenol manufactured by ACROS Organics), in which an unsaturated bond(s) of the straight-chain hydrocarbon moiety of cardanol are hydrogenated, was used as a raw material. The phenolic hydroxy group of the cardanol was reacted with monochloroacetic acid to add a carboxyl group to obtain carboxylated and hydrogenated cardanol. More specifically, the carboxylated and hydrogenated cardanol was prepared in accordance with the following procedure.

First, hydrogenated cardanol (80 g (0.26 mol)) was dissolved in methanol (120 mL). To this, an aqueous solution dissolving sodium hydroxide (64 g (1.6 mol)) in distilled water (40 mL) was added. Thereafter, at room temperature, a solution of monochloroacetic acid (66 g (0.70 mol)) manufactured by Kanto Chemical Co., Inc. dissolved in methanol (50 mL) was added dropwise. After completion of the dropwise addition, the reaction solution was continuously stirred while refluxing at 73° C. for 4 hours. The reaction solution was cooled to room temperature and the reaction mixture was acidified with a diluted hydrochloric acid until pH became 1. To this, methanol (250 mL) and diethyl ether (500 mL) and further distilled water (200 mL) were added. The resultant water layer was separated by a separating funnel and discarded. The ether layer was washed twice with distilled water (400 mL). To the ether layer, magnesium anhydride was added to dry the ether layer and then separated by filtration. The filtrate (ether layer) was concentrated by an evaporator (90° C./3 mmHg) under reduced pressure to obtain a yellow brown powdery crude product as the residue. The crude product was recrystallized from n-hexane and dried under vacuum to obtain white powder of carboxylated and hydrogenated cardanol (46 g (0.12 mol)).

The carboxylated and hydrogenated cardanol thus prepared was allowed to bind to cellulose (trade name: KC Flock W-50G manufactured by Nippon Paper Chemicals) to obtain grafted cellulose. More specifically, the grafted cellulose was prepared in accordance with the following procedure.

Cellulose (2.5 g (hydroxy-group amount: 47 mmol)) was suspended in methanol (100 mL) and stirred for one hour at room temperature and filtrated by suction. The solid substance separated by filtration was allowed to swell with dimethylacetamide (DMAc)(100 mL), stirred one hour at room temperature and filtrated by suction to remove the solvent. Thereafter, swelling with DMAc and solvent removal by suction filtration were repeated three times in the same manner. LiCl (21 g) was dissolved in DMAc (250 mL) and the DMAc-swollen cellulose previously obtained was mixed and stirred at room temperature overnight to obtain a cellulose solution. To the cellulose solution thus obtained, a DMAc solution (20 mL) dissolving the carboxylated and hydrogenated cardanol (17.3 g (46.5 mmol)), pyridine (11.0 g (140 mmol)) and tosyl chloride (8.8 g (46 mmol)) was added. The reaction solution was reacted by heating at 50° C. for one hour. The reaction solution was added dropwise to methanol (2 L) to allow reprecipitation. The resultant solid substance was separated by filtration, washed three times with methanol (500 mL) and dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose (10.4 g). DS_{CD} was obtained from the yield, and DS_{CD} was 1.49. Furthermore, the sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 104.

Reference Comparative Example 1

The same cellulose acetate before grafting as that used in Reference Example 1 was used as a comparative sample.

The cellulose acetate was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Note that the cellulose acetate did not melt even if heated and did not exhibit thermoplasticity. Furthermore, since the cellulose acetate could not be molded, a bending test was not performed.

Reference Comparative Example 2

To the same cellulose acetate before grafting as that used in Reference Example 1, triethyl citrate (trade name: Citroflex-2 manufactured by Pfizer Inc.) was added as a plasticizer such that the content became 45% by mass based on the whole resin composition. This was mixed by an extruder mixer (HAAKE MiniLab Rheomex extruder (Model CTW5, Thermo Electron Corp., Waltham, Mass.)) at a temperature of 200° C. and a screw rotation speed of 60 rpm to prepare a cellulose acetate resin composition.

The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 3

A cellulose acetate resin composition was prepared in accordance with the same content and manner as in Reference Comparative Example 2 except that the addition amount of triethyl citrate was set to 56% by mass based on the whole resin composition.

The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 4

A cellulose acetate resin composition was prepared in accordance with the same content and manner as in Reference Comparative Example 2 except that the addition amount of triethyl citrate was set to 34% by mass based on the whole resin composition.

The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 5

Phenylpropionyl chloride (PPA) was used as a reactive hydrocarbon and allowed to bind to cellulose acetate (trade name: LM-80, manufactured by Daicel Chemical Industries, Ltd., the number of acetic acid molecules added to a single glucose unit of cellulose (degree of acetylation: DS_{Ace})=2.1) to obtain grafted cellulose acetate. More specifically, the grafted cellulose acetate was prepared in accordance with the following procedure.

Cellulose acetate (10 g (hydroxy-group amount: 0.036 mol)) was dissolved in dehydrated dioxane (200 mL). To this, triethylamine (5.0 ml (0.036 mol)) was added as a reaction catalyst and an acid trapping agent. To the solution, a dioxane solution (100 mL) dissolving phenylpropionyl chloride (PPA)(10 g (0.060 mol)) manufactured by Tokyo Kasei Kogyo Co., Ltd., was added. The reaction solution was heated to reflux at 100° C. for one hour. The reaction solution was slowly added dropwise to methanol (3 L) while stirring to allow reprecipitation. The resultant solid substance was separated by filtration, dried overnight in the air and further dried under vacuum at 105° C. for 5 hours to obtain grafted cellulose acetate (12 g).

The obtained sample (grafted cellulose acetate) was measured by ¹H-NMR (product name: AV-400, 400 MHz, manufactured by Bruker), and DS_{PPA} was 0.47.

The sample was evaluated in the same manner as in Reference Example 1. The results are shown in Table 101C.

Note that the cellulose acetate did not melt even if heated and did not exhibit thermoplasticity. Furthermore, since the cellulose acetate could not be molded, a bending test was not performed.

Reference Comparative Example 6

The same cellulose acetate before grafting (DS_{Ace} =2.4) as that used in Reference Example 21 was used as a comparative sample.

The cellulose acetate was evaluated in the same manner as in Reference Example 1. The results are shown in Table 102.

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Note that the cellulose acetate did not melt even if heated and did not exhibit thermoplasticity. Furthermore, since the cellulose acetate could not be molded, a bending test was not performed.

Reference Comparative Example 7

To the same cellulose acetate ($DS_{ace}=2.4$) before grafting as that used in Reference Example 21, triethyl citrate (trade name: Citroflex-2 manufactured by Pfizer Inc.) was added as a plasticizer such that the content became 20% by mass based on the whole resin composition. This was mixed by an extruder mixer (HAAKE MiniLab Rheomex extruder (Model CTW5, Thermo Electron Corp., Waltham, Mass.)) at a temperature of 190° C. and a screw rotation speed of 60 rpm) to prepare a cellulose acetate resin composition.

The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 102.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 8

A cellulose acetate resin composition was prepared in accordance with the same content and manner as in Reference Comparative Example 7 except that the addition amount of triethyl citrate was set to 40% by mass based on the whole resin composition.

The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Examples 9 and 10

The same cellulose acetate butyrate and cellulose acetate propionate before grafting as those that used in Reference Examples 23 and 24 were used as comparative samples respectively.

The cellulose acetate butyrate and cellulose acetate propionate were evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Note that the cellulose acetate butyrate and cellulose acetate propionate melted when heated. They had thermoplasticity; however, melt viscosity was extremely large. Since it was difficult to mold them, a bending test was not performed.

Reference Comparative Examples 11 and 12

To each of the same cellulose acetate butyrate and cellulose acetate propionate before grafting as those used in Reference Examples 23 and 24 respectively, triethyl citrate (trade name: Citroflex-2 manufactured by Pfizer Inc.) was added as a plasticizer such that the content became 27% by mass based on the whole resin composition. This was mixed by an extruder mixer (HAAKE MiniLab Rheomex extruder (Model CTW5, Thermo Electron Corp., Waltham, Mass.)) at a temperature of

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180° C. and a screw rotation speed of 60 rpm to prepare a cellulose acetate butyrate resin composition and a cellulose acetate propionate resin composition.

The resin compositions were evaluated in the same manner as in Reference Example 1. The results are shown in Table 103.

Note that when each of the resin compositions was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 13

To compare with Reference Example 26, a resin composition composed of cellulose acetate and triethyl citrate as a plasticizer was prepared in accordance with the same manner as in Reference Comparative Example 2 except that the addition amount of the plasticizer was changed to 63% by mass based on the whole resin composition. The total amount of plasticizer and acetyl group was set to be equal to the amount of cardanol of Reference Example 26. The resin composition was evaluated in the same manner as in Reference Example 1. The results are shown in Table 104.

Note that when the resin composition was casted, a phase separation occurred and a uniform film could not be prepared. Thus, a tensile test was not performed.

Reference Comparative Example 14

An unsaturated bond of cardanol represented by the above Formula (2)(LB-7000: a mixture of 3-pentadecylphenol (about 5%), 3-pentadecylphenol monoene (about 35%), 3-pentadecylphenol diene (about 20%), 3-pentadecylphenol triene (about 40%); manufactured by Tohoku Chemical Industries, Ltd.) was chemically bound to a hydroxy group of a cellulose (trade name: KC Flock W-50G manufactured by Nippon Paper Chemicals) to obtain cardanol-grafted cellulose. More specifically, the cardanol-grafted cellulose was prepared in accordance with the following procedure.

In a dry box, a reaction solvent was prepared from boron-trifluoride diethyl ether ($BF_3 \cdot OEt_2$) (manufactured by Kanto Chemical Co., Inc.)(80 mL) and methylene chloride (100 mL) (manufactured by Kanto Chemical Co., Inc.) under a nitrogen gas atmosphere. To this, cellulose (2 g) was added and the mixture was stirred at room temperature for 2 hours. Thereafter, the cellulose was separated by filtration from the reaction solvent and dried under vacuum. Thereafter, to this, liquid-state cardanol (LB-7000)(100 mL) as mentioned above was added and a grafting reaction was performed while stirring at room temperature for 3 hours. After completion of the reaction, a product was separated by filtration, washed with acetone, extracted by Soxhlet and dried under vacuum at 105° C. for 5 hours to obtain a desired cardanol-grafted cellulose composition (2.5 g). DS_{CD} was obtained from a yield, and DS_{CD} was 0.16.

Note that the composition did not melt even if heated and did not exhibit thermoplasticity. Furthermore, since the composition could be neither molded nor casted, evaluation, such as a bending test and tensile test, was not performed.

TABLE 101A

		Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5	Reference Example 6
Amount of acetyl group	DS _{Ace}	2.1	2.1	2.1	2.1	2.1	2.1
	Mass fraction (%)	16	20	21	21	23	26
Amount of cardanol derivative	DS _{CD}	0.90	0.55	0	0	0	0
	modified with succinic acid						
	DS _{CD}	0	0	0.55	0.80	0.44	0.30
	modified with monochloro acetic acid						
	Mass fraction (%)	56	46	43	53	38	29
Amount of reactive hydrocarbon compound	DS _{XX}	0	0	0	0	0	0
	Mass fraction (%)	0	0	0	0	0	0
Addition amount of plasticizer (% by mass)		0	0	0	0	0	0
Bending strength (MPa)		38	48	50	36	60	83
Bending elastic modulus (GPa)		0.80	1.1	1.2	0.80	1.4	1.9
Bend-breaking strain (%)		>10	>10	>10	>10	>10	>10
Tensile strength (MPa)		29	36	38	27	45	59
Tensile elastic modulus (GPa)		0.6	0.9	1.0	0.6	1.2	1.7
Tensile breaking strain (%)		57	55	53	57	51	48
Glass transition temperature (° C.) (heat resistance)		125	134	147	139	142	150
Thermoplasticity (press moldability)		○	○	○	○	○	○
Water absorption rate (%)		1.1	1.5	1.2	0.94	1.3	1.7
Plant component ratio (%)		71	70	73	76	72	71

TABLE 101B

		Reference Example 7	Reference Example 8	Reference Example 9	Reference Example 10	Reference Example 11
Amount of acetyl group	DS _{Ace}	2.1	2.1	2.1	2.1	2.1
	Mass fraction (%)	25	26	21	24	25
Amount of cardanol derivative	DS _{CD}	0	0	0	0	0
	modified with succinic acid					
	DS _{CD}	0.30	0.22	0.44	0.24	0.30
	modified with monochloro acetic acid					
	Mass fraction (%)	28	22	36	22	29
Amount of reactive hydrocarbon compound	DS _{XX}	xx = BC	xx = BC	xx = BC	xx = BC	xx = BC
	Mass fraction (%)	0.14	0.27	0.22	0.42	0.07
	Mass fraction (%)	4.0	8.0	5.4	12	1.8
Addition amount of plasticizer (% by mass)		0	0	0	0	0
Bending strength (MPa)		113	118	106	112	94
Bending elastic modulus (GPa)		2.2	2.6	2.1	2.2	1.9
Bend-breaking strain (%)		>10	>10	>10	>10	>10
Tensile strength (MPa)		69	72	66	70	64
Tensile elastic modulus (GPa)		1.6	1.8	1.6	1.6	1.5
Tensile breaking strain (%)		48	47	52	47	50
Glass transition temperature (° C.) (heat resistance)		154	155	144	156	152
Thermoplasticity (press moldability)		○	○	○	○	○
Water absorption rate (%)		1.3	1.6	1.1	1.2	1.4
Plant component ratio (%)		68	64	68	61	69

		Reference Example 12	Reference Example 13	Reference Example 14	Reference Example 15	Reference Example 16
Amount of acetyl group	DS _{Ace}	2.1	2.1	2.1	2.1	2.1
	Mass fraction (%)	31	24	20	18	20
Amount of cardanol derivative	DS _{CD}	0	0	0	0	0
	modified with succinic acid					
	DS _{CD}	0.08	0.27	0.40	0.55	0.30
	modified with monochloro acetic acid					
	Mass fraction (%)	9.4	25	30	39	23
Amount of reactive hydrocarbon compound	DS _{XX}	xx = BC	xx = BAA	xx = BAA	xx = BAA	xx = BAA
	Mass fraction (%)	0.16	0.15	0.40	0.28	0.52
	Mass fraction (%)	5.7	7.3	16	11	21

TABLE 101B-continued

Addition amount of plasticizer (% by mass)	0	0	0	0	0
Bending strength (MPa)	95	106	107	93	95
Bending elastic modulus (GPa)	2.9	2.5	2.0	1.9	2.1
Bend-breaking strain (%)	6.5	>10	>10	>10	>10
Tensile strength (MPa)	75	65	65	63	64
Tensile elastic modulus (GPa)	1.9	1.8	1.5	1.4	1.6
Tensile breaking strain (%)	30	45	46	48	45
Glass transition temperature (° C.)	158	148	150	142	147
(heat resistance)					
Thermoplasticity (press moldability)	○	○	○	○	○
Water absorption rate (%)	1.9	1.0	0.72	0.68	0.65
Plant component ratio (%)	62	65	60	66	55

TABLE 101C

	Reference Example 17	Reference Example 18	Reference Example 19	Reference Example 20	Reference Comparative Example 1
Amount of acetyl group	DS _{Ace}	2.1	2.1	2.1	2.1
Mass fraction (%)	26	27	26	22	36
Amount of cardanol derivative	DS _{CD}	0	0	0	0
modified with succinic acid					
DS _{CD}	0.17	0.13	0.20	0.30	0
modified with monochloro acetic acid					
Mass fraction (%)	17	13	20	25	0
Amount of reactive hydrocarbon compound	DS _{XX}	xx = PPA	xx = CHC	xx = BCC	0
Mass fraction (%)	0.25	0.35	0.22	0.30	0
Addition amount of plasticizer (% by mass)	9.7	14	7.1	13	0
Bending strength (MPa)	0	0	0	0	0
Bending elastic modulus (GPa)	106	108	111	109	—
Bend-breaking strain (%)	2.5	2.6	2.5	2.5	—
Tensile strength (MPa)	>10	>10	>10	>10	—
Tensile elastic modulus (GPa)	65	66	68	67	60
Tensile breaking strain (%)	1.4	1.4	1.6	1.5	2.3
Glass transition temperature (° C.)	60	58	55	50	9.0
(heat resistance)	143	142	146	150	227
Thermoplasticity (press moldability)	○	○	○	○	X
Water absorption rate (%)	1.9	1.8	1.8	1.4	17
Plant component ratio (%)	61	58	64	65	64

	Reference Comparative Example 2	Reference Comparative Example 3	Reference Comparative Example 4	Reference Comparative Example 5
Amount of acetyl group	DS _{Ace}	2.1	2.1	2.1
Mass fraction (%)	20	16	24	29
Amount of cardanol derivative	DS _{CD}	0	0	0
modified with succinic acid				
DS _{CD}	0	0	0	0
modified with monochloro acetic acid				
Mass fraction (%)	0	0	0	0
Amount of reactive hydrocarbon compound	DS _{XX}	0	0	xx = PPA
Mass fraction (%)	0	0	0	0.47
Addition amount of plasticizer (% by mass)	0	0	0	20
Bending strength (MPa)	45	56	34	0
Bending elastic modulus (GPa)	15	11	24	—
Bend-breaking strain (%)	0.41	0.29	0.72	—
Tensile strength (MPa)	>10	>10	>10	—
Tensile elastic modulus (GPa)	—	—	—	52
Tensile breaking strain (%)	—	—	—	1.9
Glass transition temperature (° C.)	—	—	—	16
(heat resistance)	40	25	71	152
Thermoplasticity (press moldability)	○	○	○	X
Water absorption rate (%)	5.1	4.3	5.7	4.5
Plant component ratio (%)	35	28	42	51

TABLE 102

		Reference Example 21	Reference Example 22	Reference Comparative Example 6	Reference Comparative Example 7	Reference Comparative Example 8
Amount of acetyl group	DS _{Ace}	2.4	2.4	2.4	2.4	2.4
Amount of cardanol derivative	Mass fraction (%)	31	24	31	39	24
	DS _{CD}	0.19	0.50	0	0	0
	modified with monochloro acetic acid					
	Mass fraction (%)	20	40	0	0	0
Addition amount of plasticizer (% by mass)		0	0	0	20	40
Bending strength (MPa)		120	59	—	50	20
Bending elastic modulus (GPa)		2.8	1.5	—	2.3	0.80
Bend-breaking strain (%)		>10	>10	—	>10	>10
Tensile strength (MPa)		55	38	58	—	—
Tensile elastic modulus (GPa)		1.8	1.0	2.1	—	—
Tensile breaking strain (%)		34	53	11	—	—
Glass transition temperature (° C.) (heat resistance)		154	134	216	90	63
Thermoplasticity (press moldability)		○	○	X	○	○
Water absorption rate (%)		2.1	1.2	9.0	3.1	2.6
Plant component ratio (%)		66	71	61	49	36

TABLE 103

		Reference Example 23	Reference Example 24	Reference Example 25	Reference Comparative Example 9	Reference Comparative Example 10	Reference Comparative Example 11	Reference Comparative Example 12
Amount of acetyl group	DS _{Ace}	1.0	0.18	0.18	1.0	0.18	1.0	0.18
	Mass fraction (%)	9.8	1.8	2.0	13	2.5	9.8	1.8
Amount of butyryl/propionyl group	DS _{Bu} or DS _{Pr}	DS _{Bu}	DS _{Pr}	DS _{Pr}	DS _{Bu}	DS _{Pr}	DS _{Bu}	DS _{Pr}
		1.66	2.49	2.49	1.66	2.49	1.66	2.49
Amount of cardanol derivative	Mass fraction (%)	27	27	36	37	46	27	34
	DS _{CD}	0.34	0.33	0.21	0	0	0	0
	modified with monochloro acetic acid							
	Mass fraction (%)	27	27	19	0	0	0	0
Amount of reactive hydrocarbon compound	DS _{XX}	0	0	xx = BC	0	0	0	0
				0.10				
	Mass fraction (%)	0	0	2.7	0	0	0	0
Addition amount of plasticizer (% by mass)		0	0	0	0	0	27	27
Bending strength (MPa)		45	49	60	—	—	23	15
Bending elastic modulus (GPa)		1.3	1.4	1.6	—	—	0.79	0.82
Bend-breaking strain (%)		>10	>10	>10	—	—	>10	>10
Tensile strength (MPa)		35	39	43	36	40	—	—
Tensile elastic modulus (GPa)		0.85	0.87	1.0	1.0	1.1	—	—
Tensile breaking strain (%)		100	98	82	55	52	—	—
Glass transition temperature (° C.) (heat resistance)		94	92	100	135	143	59	59
Thermoplasticity (press moldability)		○	○	○	Δ	Δ	○	○
Water absorption rate (%)		0.65	0.76	0.74	2.6	3.1	1.5	1.6
Plant component ratio (%)		60	61	57	50	52	36	38

TABLE 104

		Reference Example 26	Reference Comparative Example 13
Amount of cellulose	Mass fraction (%)	24	24
Amount of acetyl group	DS _{Ace}	0	2.1
	Mass fraction (%)	0	13
Amount of cardanol derivative	DS _{CD}	1.49	0
	modified with monochloro acetic acid		
	Mass fraction (%)	76	0
Addition amount of plasticizer (% by mass)		0	63
Bending strength (MPa)		25	9
Bending elastic modulus (GPa)		0.38	0.20
Bend-breaking strain (%)		>10	>10
Tensile strength (MPa)		17	—

TABLE 104-continued

	Reference Example 26	Reference Comparative Example 13
Tensile elastic modulus (GPa)	0.26	—
Tensile breaking strain (%)	22	—
Glass transition temperature (° C.) (heat resistance)	84	21
Thermoplasticity (press moldability)	○	○
Water absorption rate (%)	1.9	4.0
Plant component ratio (%)	89	24

When Reference Examples 1 to 6 are compared to Reference Comparative Example 1, the cardanol-grafted cellulose resins (an acetyl group is also added to a cellulose hydroxy group) of the reference examples each had thermoplasticity

(press moldability) and excellent bending properties without reducing a plant component ratio, and further tensile properties (particularly, breaking strain) and water resistance (water absorption rate) were improved, compared to the cellulose derivative (cellulose acetate) before grafting which had no thermoplasticity. Furthermore, when Reference Examples 1 to 6 are compared to Reference Comparative Examples 2 to 4, the cardanol-grafted cellulose resins (an acetyl group is also added to a cellulose hydroxy group) of the reference examples were more improved in bending properties, tensile properties and water resistance than the cellulose derivatives before grafting (cellulose acetate) which contained the plasticizer. In addition, high heat resistance (glass transition temperature) was obtained without reducing the plant component ratio.

As shown in Reference Examples 7 to 20, bending properties (particularly, bending strength) and tensile properties (particularly, tensile strength) can be even more improved while obtaining high water resistance by grafting with not only cardanol but also a reactive hydrocarbon.

In Reference Examples 21 and 22 and Reference Comparative Examples 6 to 8, compared to Reference Examples 1 to 20 and Reference Comparative Examples 1 to 5, the amount of acetyl group added to a hydroxy group of cellulose is increased. Even in these case, when Reference Examples 21 and 22 are compared to Reference Comparative Example 6, the cardanol-grafted cellulose resins of the reference examples each had thermoplasticity and excellent bending properties without reducing a plant component ratio, and further tensile properties (particularly, breaking strain) and water resistance were improved, compared to the cellulose derivative before grafting which had no thermoplasticity. Furthermore, when Reference Examples 21 and 22 are compared to Reference Comparative Examples 7 and 8, the cardanol-grafted cellulose resins of the reference examples were more improved in bending properties (particularly, bending strength), tensile properties and water resistance than the cellulose derivatives before grafting which contained the plasticizer. In addition, high heat resistance was obtained without reducing the plant component ratio.

As shown in Reference Comparative Examples 2 to 4, 7 and 8 containing plasticizer, excellent heat resistance was not obtained by adding the plasticizer alone. According to the reference examples, not only thermoplasticity can be imparted to a cellulose resin but also excellent heat resistance can be obtained.

Furthermore, as shown in Reference Comparative Example 5 in which a reactive hydrocarbon alone was grafted, thermoplasticity was not obtained only by grafting a reactive hydrocarbon alone, and bending properties, tensile properties (particularly, breaking strain) and water resistance were not improved. According to the reference example, not only thermoplasticity can be imparted to a cellulose resin but also excellent bending properties, tensile properties (particularly, breaking strain) and water resistance can be obtained.

Reference Examples 23 to 25 and Reference Comparative Examples 9 to 12, each are an example of a cellulose resin prepared by using a cellulose derivative having not only an acetyl group but also a butyryl group or a propionyl group added to a hydroxy group. Even in these case, when Reference Examples 23 to 25 are compared to Reference Comparative Examples 9 and 10, in the cardanol-grafted cellulose resins of the reference examples, excellent thermoplasticity and bending properties were obtained without reducing the plant component ratio, and further tensile properties (particularly breaking strain) and water resistance were improved, compared to the cellulose derivatives before grafting. Fur-

thermore, when Reference Examples 23 to 25 and Reference Comparative Examples 11 and 12 are compared, the cardanol-grafted cellulose resins of the reference examples were more improved in bending properties (particularly, bending strength), tensile properties and water resistance than the cellulose derivatives before grafting which contained the plasticizer. In addition, high heat resistance was obtained without reducing the plant component ratio.

Reference Example 26 is an example of a cellulose resin prepared by using cellulose having a hydroxy group of cellulose to which an acyl group such as an acetyl group is not added. Even in this case, when Reference Example 26 is compared to Reference Comparative Example 13, the cardanol-grafted cellulose resin of the reference example was more improved in bending properties (particularly, bending strength), tensile properties and water resistance than the cellulose derivative of Reference Comparative Example 13, in which the cellulose derivative (cellulose acetate) contained a plasticizer (the weight ratio of the cellulose component is the same as the Reference Example 26). In addition, high heat resistance was obtained without reducing the plant component ratio.

As described above, according to the reference examples, it is possible to provide a cellulose resin improved in water resistance and having good thermoplasticity (press moldability) and sufficient heat resistance while maintaining a high plant component ratio (high vegetism). Furthermore, a press molded product having high bending properties can be obtained and a film molded product can be improved in tensile properties (particularly, toughness). Furthermore, according to the reference examples, a grafted cellulose resin having a high plant component ratio as well as high utilization ratio of non-edible parts can be obtained.

While the present invention has been described with reference to the exemplary embodiments and examples, the present invention is not limited to the above exemplary embodiments and examples. Various changes that can be understood by those skilled in the art may be made to the constitution and details of the present invention within the scope thereof.

This application claims the right of priority based on Japanese Patent Application No. 2011-082978 filed on Apr. 4, 2011, the entire content of which is incorporated herein by reference.

The invention claimed is:

1. A cellulose resin produced by binding cellulose or a derivative thereof and cardanol or a derivative thereof by using a hydroxy group of the cellulose or a derivative thereof and a hydroxy group of the cardanol or a derivative thereof, wherein carbon atoms to which the hydroxy groups are bound are mutually linked via a carbonate bond or urethane bond formed by using the hydroxy groups.
2. The cellulose resin according to claim 1, wherein the number of the cardanol or a derivative thereof added to the cellulose or a derivative thereof per glucose unit thereof, DS_{CD} , is 0.1 or more.
3. The cellulose resin according to claim 2, wherein the number of remaining hydroxy groups per glucose unit of the cellulose or a derivative thereof, DS_{OH} , is 0.9 or less.
4. The cellulose resin according to claim 2, including an acyl group added to a hydroxy group of a glucose unit of the cellulose or a derivative thereof.
5. The cellulose resin according to claim 2, wherein the cardanol or a derivative thereof is hydrogenated cardanol obtained by hydrogenating cardanol.
6. A resin composition containing the cellulose resin according to claim 2 as a base resin.

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7. The cellulose resin according to claim 1, wherein the number of remaining hydroxy groups per glucose unit of the cellulose or a derivative thereof, DS_{OH} , is 0.9 or less.

8. The cellulose resin according to claim 7, including an acyl group added to a hydroxy group of a glucose unit of the cellulose or a derivative thereof.

9. The cellulose resin according to claim 7, wherein the cardanol or a derivative thereof is hydrogenated cardanol obtained by hydrogenating cardanol.

10. A resin composition containing the cellulose resin according to claim 7 as a base resin.

11. The cellulose resin according to claim 1, including an acyl group added to a hydroxy group of a glucose unit of the cellulose or a derivative thereof.

12. The cellulose resin according to claim 11, wherein the cardanol or a derivative thereof is hydrogenated cardanol obtained by hydrogenating cardanol.

13. A resin composition containing the cellulose resin according to claim 11 as a base resin.

14. The cellulose resin according to claim 1, wherein the cardanol or a derivative thereof is hydrogenated cardanol obtained by hydrogenating cardanol.

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15. A resin composition containing the cellulose resin according to claim 14 as a base resin.

16. A resin composition containing the cellulose resin according to claim 1 as a base resin.

17. A molding material comprising the resin composition according to claim 16.

18. A method for producing a cellulose resin, comprising: converting a hydroxy group of cardanol or a derivative thereof into a chloroformate group or an isocyanate group to form a modified cardanol, and reacting the chloroformate group or isocyanate group of the modified cardanol with a hydroxy group of cellulose or a derivative thereof to bind the modified cardanol to the cellulose or a derivative thereof.

19. The method for producing a cellulose resin according to claim 18, wherein the cellulose or a derivative thereof is a cellulose derivative obtained by adding an acyl group to a part of the hydroxy groups.

20. The method for producing a cellulose resin according to claim 18, wherein the cardanol or a derivative thereof is hydrogenated cardanol obtained by hydrogenating cardanol.

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